THE SOLUBILITY OF GASES IN LIQUIDS

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Received October 25, 1965

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I. Introduction

The solubility of gases in liquids has been under quantitative investigation since the beginning of the nineteenth century. The last decade has seen some remarkable advances in theory, empirical correlations, systems studied, and apparatus. Much of the earlier work was more qualitative than quantitative. Gas solubilities have become increasingly more important for both the theoretical understanding of the liquid state and solutions, and for practical applications from the solubility of gases in human tissues to the solubility of gases in molten salts and metals.

This review brings up to date the earlier comprehensive review of Markham and Kobe (393). An annotated bibliography (1907–1941) on the solubility of Ar, CO_2, He, and N_2 in organic liquids was prepared by Croxton (115). The two books by Hildebrand and Scott (243, 244) contain chapters on gas solubility and many references. There are other papers containing either general correlations or many references (170, 206, 247, 248, 282, 353, 373, 485, 670). The review by Himmelblau (249) on the diffusion of dissolved gases in

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liquids is of interest, and the review by Rowlinson and Richardson (509) on the solubility of solids in compressed gases may interest some readers. The limited literature on the solubility of liquids in compressed gases has yet to be reviewed.

The literature since Markham and Kobe was searched and critically evaluated. The principal medium of the search was *Chemical Abstracts* through Vol. 59, or the end of 1963. All pertinent articles abstracted through the end of 1963 were included, although many articles which were published in 1964 and 1965 were also included. Where the original paper was not examined, a *Chemical Abstracts* reference is supplied in the list of references.

The emphasis in this review was placed on physical methods of determining solubilities and on reporting and discussing only equilibrium or saturation solubilities. Thus, the vast literature on the analysis of gases absorbed in liquids was ignored. Since most of these analyses involve chemical methods, the latter was also ignored except for oxygen in water. The extensive literature on the solubility of gases in ponds, streams, and ground waters was not included because of the equilibrium criterion.

There is an almost nonexistent dividing line between gas solubility (in liquids) and vapor–liquid equilibrium, especially at elevated pressures. The solubility of the vapors of some substances was included where the experimental conditions were such that the pressure was lower than the normal vapor pressure. Also included are: (a) solubilities of gases in molten metals, alloys, salts, and glasses; (b) solubilities of gas mixtures; (c) solubility in tissues and some biological systems; (d) solubility nomographs; and (e) partial molal volumes of gases in liquids.

The large body of literature on the solubility of gases in plastic materials was excluded since much of this data is for plastic films. The solubility of gases in solids and substances whose composition would tend to be indeterminable (like molten slags) was also excluded.

II. NOMENCLATURE

The system of notation used in this review follows. Some specialized symbols which apply to a particular approach, and where we wished to use the author's own notation for clarity, are defined where they are used.

Upper Case Symbols

A	arbitrary constant
C_l, C_d	concentration of gas dissolved in the liquid phase
C_g	concentration of gas dissolved in the gas phase
C_w	weight solubility (see section IVD)
ΔC_p	heat capacity change on solution
ΔE^v	molar energy of vaporization
$\bar{G}$	molar Gibbs free energy
H_2	Henry's law constant (see section VD)
ΔH, $\Delta \bar{H}^\circ$	molar heat of solution
ΔH^v	molar heat of vaporization
K	Henry's law constant or Setschenow equation parameter
K_1	Henry's law constant (to fit Eq 5)
K_2	Henry's law constant (to fit Eq 6)
K_c	Henry's law constant (to fit Eq 7)
K'	Henry's law constant, modified
K_r	Henry's law constant, reduced
K°, K_s°	limiting Henry's law constants in water and in salt solution
L	Ostwald coefficient (see section IVB)
M	molecular weight
P	pressure
P_s, P°	solvent vapor pressure
P_T	total pressure
P_i	partial pressure or vapor pressure
S	Kuenen coefficient (see section IVA)
S_i°, S_i	solubility of gas in pure solvent, or salt solution
$\bar{S}_2$	partial molar entropy of gas in solution
S_2^g	molar entropy of gas in gas phase
ΔS°	molar entropy of solution
T	temperature, °K
T_c	critical temperature
T_r	reduced temperature
V, $\bar{V}$	volume, molar volume
V_s	volume of solvent
V_g	volume of gas
V_0	molar volume of gas in cc/mole at 0°
$\bar{V}_i^\circ$	partial molar volume at infinite dilution of gas
$\bar{V}_s^\circ$	partial molar volume at infinite dilution of electrolyte
X_2, X_1	mole fraction solubility of gas in solution
X_2^i	ideal mole fraction solubility of gas in solution
Y	vapor phase mole fraction

Lower Case Symbols

a, b, c	arbitrary constants
c_s	salt concentration, moles per liter
c_i	gas concentration, moles per liter
f_i°	activity coefficient of dissolved gas in salt-free solution
f_i	activity coefficient of dissolved gas in salt solution
g	gravitational constant
g_{ij}^E	excess Gibbs free energy
k	Boltzmann constant
k_s	salting-out parameter
k_x	salting-out parameter for salt x
k_i	nonelectrolyte self-interaction parameter
k_{nm}	salt-effect parameter
m	molality
p	pressure
r	radius of spherical gas atom
t	temperature, °C
u	decimal fraction of solute in solution
v	volume

Greek Letter Symbols

α	Bunsen coefficient (see section IVA)
α_{ij}	interaction parameters
β	absorption coefficient (see section IVB)
β_0	compressibility of pure solvent
γ	activity coefficient
δ	Hildebrand solubility parameter
ϵ/k	Lennard-Jones force constant
ϕ	volume fraction or vapor phase activity coefficient
ρ	density
σ	surface tension

III. METHODS AND APPARATUS

The variety of approaches which have been used to determine the solubility of gases in liquids is an adequate testimonial to man's ingenuity. The equipment used ranges in complexity and cost from mass spectrometers to the simple van Slyke apparatus, in time from minutes to many hours, and in precision from the purely qualitative to the highly precise.

Primarily physical methods will be discussed in this section, although, in specific instances chemical methods are sometimes more precise. There are several reasons for omitting chemical methods (except for oxygen in water). First, they are normally specific for a particular gas and thus do not show general applicability. Second, it is quite difficult to distinguish between "(chemical) absorption" methods and those which involve purely equilibrium solubilities. The literature for the analysis of dissolved gases was in general ignored. Third, gas absorption studies usually involve complex chemical equilibriums, and, since their purpose is to study the chemical equilibrium involved, the result frequently is that insufficient information is available to properly evaluate the study as an equilibrium gas solubility.

Physical methods can be divided into two broad classifications: saturation methods in which a previously degassed solvent is saturated with a gas under conditions where appropriate volumes, pressures, and temperatures may be determined; and extraction methods where the dissolved gas in a previously saturated solution is removed under conditions where appropriate P, V, and T values may be evaluated. Equilibrium between the gas and liquid phases has been obtained by shaking a mixture of the two, by flowing a film or stream of the liquid through the gas, by bubbling the gas through the liquid, or by flowing the gas over the liquid held stationary on some supporting medium (as in gas–liquid partition chromatography). The determination of the quantities of the components in the gas and liquid phases has been carried out chemically, volumetrically (and with the supporting use of manometers), by mass spectrometer, and by gas–liquid partition chromatography. These methods will be discussed below.

A. MANOMETRIC–VOLUMETRIC METHODS

First, some general considerations are discussed. Cook (103, also see 104) gives an excellent analysis of the problems involved in gas solubility determinations, the magnitudes and importance of contributing factors, and his approach to achieving a truly high-precision (±0.05%) gas solubility apparatus. He is to be commended for a major contribution to gas solubility determinations.

In gas solubility determinations contributing factors like purity of materials and the measurement of the physical properties of pressure, volume, and temperature are usually adequately determined. The discrepancies, often large, between published values which appear in the literature (for example, the solubility of atmospheric gases in water and sea water continues to be measured and debated) are most probably due to other factors. Cook and Hanson (104) list these as being one or more of the following: (a) failure to attain equilibrium; (b) failure to completely degas the solvent; (c) failure to ascertain the true amount of gas dissolved; and (d) failure to make certain that the transfer of gas from a primary container to the apparatus does not involve contamination. The last two factors can be controlled by proper design, calibrations, and corrections. It is better to determine the initial quantity of gas in the dry state, *i.e.*, free of solvent, since P–V–T data can be used, especially if there is any uncertainty as to whether the gas is saturated with solvent vapor. Where known, the more accurate equations of state should be used since even at 1 atm pressure deviations from the ideal gas law can be significant. The first two factors will be discussed further.

For equilibrium solubility determinations the attainment of equilibrium is of prime importance. In flow systems the attainment of equilibrium is checked for by determining the solubility at several rates of flow. In nonflow systems the agreement between solubility determinations found with varying both the vigor of the stirring (or shaking) and the pressure of the gas above and below the equilibrium pressure serves as the main criterion. For each type of apparatus it is important to provide these checks by varying the conditions.

1. The Solubility of Oxygen in Water as a Comparison Standard

It would be a boon to workers in the field to have a reliable standard for comparison. The criteria here would be that the solvent and gas are readily available in high purity, and that at some convenient conditions a number of workers would have obtained substantially identical values having followed different approaches. The solubility of oxygen in water at 25° and 1 atm meets these criteria. There have been several recent determinations following different approaches, including both chemical and physical methods, which are in substantial agreement (152, 166, 231, 318, 424, 425, 581), and the value suggested as a standard is the Bunsen coefficient of 0.02847. Considering these seven values, the average deviation is 0.00006 in the Bunsen coefficient or 0.21%. This deviation is just about within the independent experimental error of the seven determinations. The values are summarized in Table I along with other values of interest. As a further aid Table II contains smoothed values of the solubility of O_2, N_2, and Ar in water as a function of temperature.

TABLE I

SOLUBILITY OF OXYGEN IN WATER[a]

Worker	Date	Estimated error, %	Bunsen coeff at 25°	Ref
Winkler	1889		0.02831	657
Fox	1909		0.02890	194
Morrison and Billett	1952	0.5	0.02848	428
Truesdale, *et al.*	1955	0.27	0.02800	610
Steen	1958	0.12	0.02863	581
Elmore and Hayes	1960	0.20	0.02824	166
Morris, *et al.*	1961	0.27	0.02850	425
Klots and Benson	1963	0.16	0.02848	318
Douglas	1964	0.25	0.02830	152
Montgomery, *et al.*	1964	0.26	0.02849	424
Green	1965	0.27	0.02843	231

Av (all 11) = 0.02843 Av dev (all 11) = 0.00016

[a] Recommended standard value based on the agreement attained in recent studies is **0.02847**.

2. Degassing the Solvent

The complete removal of gas from a liquid is important for saturation methods, where the solvent must be initially gas free, and for extraction methods, where the gas is to be completely extracted. The single criterion for complete degassing which has been most widely used is the reproducibility of a measurement or its corollary, the agreement between several workers for the same measurement. This criterion is open to two criticisms: (a) the repetition of systematic errors, and (b) the perpetuating of older measurements as standards when they may have been superseded by more reliable measurements.

Two additional criteria (104) for complete degassing should be mentioned. The first is a dynamic method in which a vacuum thermocouple gauge is located between the last liquid nitrogen trap (on the apparatus) and before the vacuum pump. During the degassing procedure in which the solvent is simultaneously boiled and pumped on, the vacuum gauge reading slowly falls from greater than 1000 μ to the base pressure of the pump. When the pressure is at the base pressure of the pump, this indicates that only negligible amounts

TABLE II

SOLUBILITY OF NITROGEN, OXYGEN, AND ARGON IN WATER AT 1 ATM

(Units: Bunsen Coefficient × 10^3)

Temp, °C:	0	5	10	15	20	25	30	35	40	50
Nitrogen										
Hamburg[a]	23.79	21.05	18.81	17.03	15.70	14.68	...	...	...	...
Fox[a]	23.19	20.68	18.63	17.02	15.72	14.65	13.75	12.99	12.33	11.16
Winkler[a]	23.12	20.50	18.29	16.56	15.18	14.10	13.19	12.35	11.64	10.71
Adeney and Becker[a]	...	21.22	18.70	16.96	15.55	14.35	13.27	...	...	...
Morrison and Billett[b] (428)	...	...	19.25	17.36	15.86	14.63	13.64	12.82	12.17	11.23
Douglas (152)	...	20.91	18.75	17.05	15.57	14.41	13.45	...	...	...
Klots and Benson (318)	...	21.18	18.99	17.24	15.84	14.66	13.45	...	...	...
Oxygen										
Winkler[a]	48.89	42.87	38.02	34.15	31.02	28.31	26.08	24.40	23.06	20.90
Fox[a]	49.24	43.21	38.37	34.55	31.44	28.90	26.65	24.85	23.30	20.95
Truesdale, Downing, and Lowden (610)	47.65	41.73	36.98	33.20	30.27	28.00	26.29	24.94	...	...
Elmore and Hayes (166)	49.30	43.15	38.16	34.12	30.88	28.24	25.97	...	...	...
Morrison and Billett[b] (428)	...	...	38.32	34.35	31.13	28.48	26.30	24.48	22.97	20.71
Douglas (152)	...	...	37.97	34.03	30.95	28.30	26.20	...	...	...
Steen[c] (581)	...	42.80	38.37	34.38	31.06	28.65	...	...	...	...
Klots and Benson (318)	...	43.03	38.14	34.23	31.11	28.48	...	...	...	...
Green (231)	49.43	43.31	38.39	34.39	31.12	28.43	26.23	24.40	...	...
Montgomery, Thom, and Cockburn (424)	48.19	43.04	38.13	34.21	31.06	28.49	26.41	24.70	23.31	...
Morris, Stumm, and Galal[c] (425)	49.36	43.33	38.34	34.27	31.03	28.50	26.58	...	...	...
Argon										
Estreicher[a]	57.80	50.80	45.25	40.99	37.90	34.70	32.56	30.54	28.65	25.67
Winkler[a]	53.0	...	42.0	...	35.0	...	30.0	...	27.0	...
Antropoff[a]	56.1	...	43.8	...	37.9	...	34.8	...	...	...
Lannung[a]	...	...	41.1	37.1	33.6	31.4	28.9	27.1	25.3	...
Eucken and Hertzberg (173)	52.6	...	...	...	33.6	...	...	...	...	...
Friedman (197)	...	...	...	38.2	...	31.1	...	...	...	...
Holland and Clever (260)	...	...	...	...	...	31.5	28.8	26.9	25.2	...
Morrison and Johnstone[b] (429)	...	...	41.7	36.7	33.5	30.7	28.1	26.4	24.7	22.1
Koenig (327)	...	...	37.9	35.8	32.5	...	...	...	...	...
Douglas (152)	...	46.89	41.80	37.53	34.05	31.23	28.88	...	...	...
Ben-Naim and Baer[c] (38)	53.64	47.16	41.89	37.62	34.13	31.21	28.65	...	...	...
Klots and Benson (318)	...	47.13	41.82	37.59	34.21	31.37	...	...	...	...

[a] Values as corrected for impurities and smoothed in Landolt-Bornstein, "Physikalisch-Chemische Tabellen, 1936 Edition," Edwards Brothers Printing, Ann Arbor, Mich., 1943. [b] Calculated from Morrison's equations and converted to volume of water. [c] Smoothed by us using four-constant equation.

of noncondensible gases are present. After the base pump pressure has been reached, an additional quantity of solvent should be evaporated to be doubly certain that the solvent is completely degassed. The second criterion requires cushioning the degassed solvent between mercury. If a bubble appears, the degassing operation should be repeated. This test is quite sensitive since gas bubbles much smaller than 0.001 cc can readily be detected. Since solution rates are slow, these gas bubbles will persist for several minutes.

The most frequently used method of degassing a liquid is to boil away a portion of it under vacuum. This procedure can be considered to be a batch binary distillation. The Ramsey–Rayleigh equation for this type of distillation predicts that the evaporation of as little as 0.1% of the solvent should reduce the gas content by several 1000-fold. However, this equation assumes that equilibrium conditions prevail between the gas and the liquid and under actual degassing operations this is not the case. In practice 10–20% of the solvent is evaporated, and one (or both) of the criteria mentioned in the previous paragraph should be employed.

Another degassing procedure employs the method of pumping on the frozen solvent. This procedure gives good results when it is important to minimize the loss of solvent, *but* it is necessary to repeat the process at least three times and pumping on the frozen solvent for periods of an hour or longer in each cycle. It is more important to test for completeness of degassing when employing this method than when evaporating large amounts of the liquid.

Clever, *et al.* (97), employed a method for degassing that operated in two stages. The first stage involved pumping on boiling solvent to evaporate a portion of it, and to remove perhaps 90% of the dissolved gas. Then in the second stage this preliminarily degassed liquid is sprayed through a fine nozzle into an evacuated flask. This procedure was found to give rapid and complete degassing. A similar method was employed by Baldwin and Daniel (22) where they permitted an oil sample to slowly drip into an evacuated vessel. They found that this removed 97–98% of the dissolved gas.

The technique of removing a gas completely from a liquid by stripping the liquid through bubbling an inert gas through the previously saturated liquid will be discussed in the section on gas chromatographic methods where this technique is essential to the method.

3. The Effect of Temperature on Solubility Measurements

A full analysis of the effect of temperature control on gas solubility measurements is given by Cook (103) who points out that there are four factors to consider: (a) the temperature coefficient of the solvent vapor pressure; (b) the temperature coefficient of solubility, or more realistically, the change in the equilibrium partial pressure of the dissolved gas with temperature at an approximately constant concentration; (c) the temperature level of the experiment; and (d) the pressure level of the experiment. The magnitude of these factors will be quite dependent on not only the system studied but also on the type of apparatus used. After a complete analysis of all contributing factors, Cook found that temperature control to $\pm 0.1°$ was adequate for an over-all precision of 0.05% for his apparatus for the system H_2-n-heptane in the range -30 to 50°. It would appear that temperature control of $\pm 0.1°$ should be more than adequate for most purposes.

4. The Apparatus of Cook and Hanson (103, 104)

The apparatus and procedure of Cook and Hanson will be described in somewhat more detail than other methods since they achieved an unusually high level of precision for a physical method. This apparatus is also described by Mader, Vold, and Vold (384).

The basic apparatus is shown in Figure 1. It was mounted on a steel plate which was shaken at a frequency of about 170 min^{-1} and an amplitude of about $^3/_8$ in. The shaking mechanism imparted a horizontal motion to minimize pressure disturbances due to vertical accelerations of the mercury present. The entire apparatus was housed in an air thermostat controlled to at least $\pm 0.1°$. A millimeter scale mounted on the steel plate and observed with a cathetometer provided a reference point for appropriate readings. An auxiliary gas-charging apparatus was connected to the solubility apparatus at point 12. Once the apparatus was set up and charged all manipulations were made remotely so as not to disturb the temperature equilibrium. Volumetric calibration was performed by weighing mercury displaced from pertinent sections of the apparatus which are the gas bulbs, A and C, the gas burets, B and D, and the solvent bulb, E, from point 19 down to and including the solvent buret. Also calibrated was the secondary gas buret and bulb from point 19 down to stopcock 2. The appropriate capacities of the various parts of the apparatus are: solvent bulb, 200 cc; primary gas bulb, 22 cc; secondary gas bulb, 1 cc; solvent buret, 0.1 cc/cm; primary gas buret, 0.25 cc/cm; and secondary gas buret, 0.015 cc/cm.

An outline of the procedure used follows. First, the gas and solvent bulbs are filled with mercury, and then by displacing mercury into the manometer a sufficient quantity of solvent is admitted through the joint at point 12 followed by about an inch of air to provide space for boiling the solvent. The solvent is degassed by pumping and boiling using the thermocouple gauge check described earlier, and also by checking for residual gas bubbles by confining the solvent between mercury admitted through stopcocks 3 and 6. About

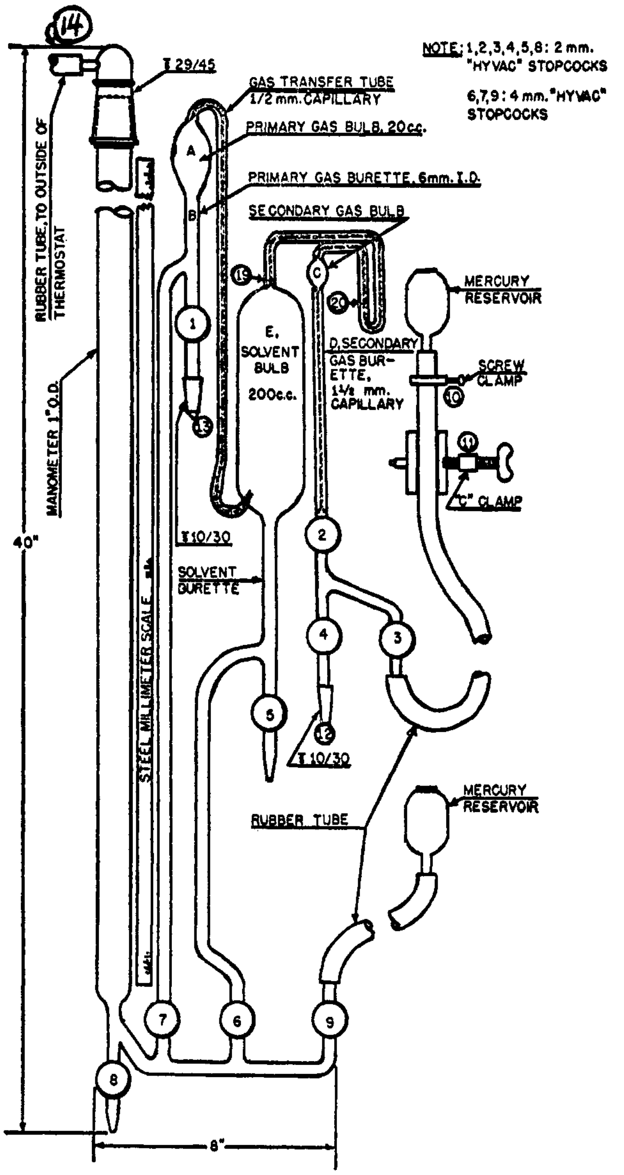

Figure 1.—The gas solubility apparatus of Cook and Hanson (103, 104). Reprinted from U. S. Atomic Energy Commission Report UCRL-2459 by permission of the author.

10–20% of the solvent is evaporated in the degassing process which takes several hours. The gas-charging system is connected at point 13, and after the system is purged and checked for tightness an appropriate quantity of gas is admitted through stopcock 1. The gas-charging system is removed and the thermostat closed and set to control at 25°. By appropriate pressure, volume, and temperature readings the quantity of gas charged may be calculated from an applicable equation of state. An interesting point here is that a change of 1–2 cm in the gas pressure can cause adiabatic heating or cooling sufficient to require an additional half-hour to attain temperature equilibrium. The gas is then completely transferred into solvent bulb E through the gas transfer tube by alternately applying vacuum through 6 and pressure through 7. Stopcock 6 is left open during the dissolution process where the entire apparatus is shaken. The initial dissolution is hastened by applying about 10 psig to the manometer. When a residual gas bubble of about 1 cc remains, it is drawn over into the secondary gas bulb and buret and its volume (which can be measured to 0.005% as a check on the rate of solution and the attainment of equilibrium) is measured. The residual gas is returned to the solvent bulb and shaking is repeated. The process is repeated until equilibrium is attained, and it is also repeated at two or more pressures as a further guarantee of attaining equilibrium. The equilibrium pressure is determined to 0.1–0.2 mm. The entire process is repeated at successive temperatures, thus yielding for a single charging a set of measurements for a range of temperatures and pressures. The solvent volume is determined at 35° by draining mercury between calibrated points on E out through 5, weighing it, and calculating the solvent volume as the difference between the calibrated volume of E and the volume of the mercury which was drained off.

The authors estimate the reproducibility as better than ±0.1% in ref 104 and better than ±0.05% in ref 103. This is by far the most precise apparatus for determining gas solubilities by physical methods reported to date. A serious disadvantage is that a good estimate of the solubility must be known beforehand since the apparatus is designed such that 95% of the gas should be absorbed. The size of the solvent bulb E would have to be changed for different systems (or ranges of solubility). This disadvantage is partially offset by permitting the reasonably large pressure range of 0.5–1.5 atm to be available through the manometer.

5. *Saturation Methods*

The apparatus (Figure 2) designed by Morrison and Billett (427) was based on attaining saturation by flowing a liquid film through the gas. A modification of this design (for full details see ref 32) was used by Clever and co-workers (95–98), Saylor and Battino (530), and Koenig (327). The degassed solvent in M is injected drop by drop through A and flows in a thin film down the absorption spiral B and into gas buret C. The absorption section is initially charged with gas. Saturated solvent flows out of E at such a rate that the levels in C and in the leveling buret D are kept the same. Solvent from E is collected and measured. Readings of C give the volume of gas dissolved, while the volume of solvent is the amount collected at E together with the volume accumulating in C and D. The absorption section is thermostated. For high solubility gases an additional gas buret is sealed into the system above spiral B. The variation of the flow rate within wide limits had no appreciable effect on the solubility. The reproducibility was ±0.5%. A disadvantage of this apparatus is that normally only one gas in one solvent at one temperature and one pressure can be made on a single charging of the apparatus.

The dissolution vessel and connections for the apparatus of Ben-Naim and Baer (38) is shown in Figure 3. Degassed solvent is transferred to the previously evacuated vessel A through point D. This vessel is connected to a gas buret and manometer at point C and all of these parts are immersed in a water thermostat (±0.03°) with a window for viewing. The solvent fills A entirely and the liquid levels are in the capillaries h, l, and k when the system is charged with solvent saturated gas. Appropriate readings on the manometer, gas buret, and dissolution vessel are recorded. Dissolution of the gas is caused by switching on a magnetic stirrer which forces liquid up through capillaries h and k into bulbs a and b. The gas enters A through the capillary l and dissolves at the cone-shaped interface which is formed. At an initial high stirring rate some solvent is forced through m into A and within 2-3 min about 99% of the gas has dissolved. Equilibrium takes an additional 4 hr to achieve with gentle stirring. The over-all precision is estimated as ±0.2%.

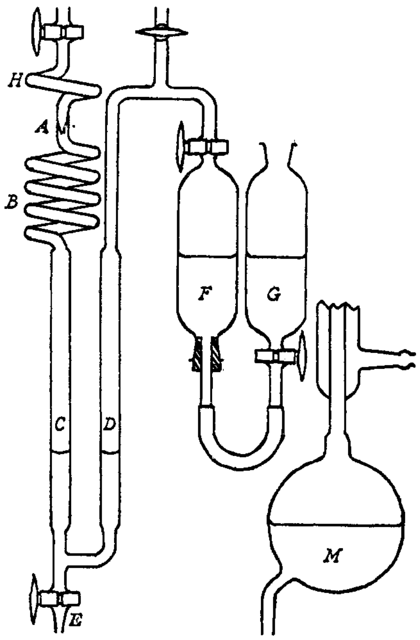

Figure 2.—The gas solubility apparatus of Morrison and Billett (427). Reprinted from the *Journal of the Chemical Society* by permission of the Chemical Society.

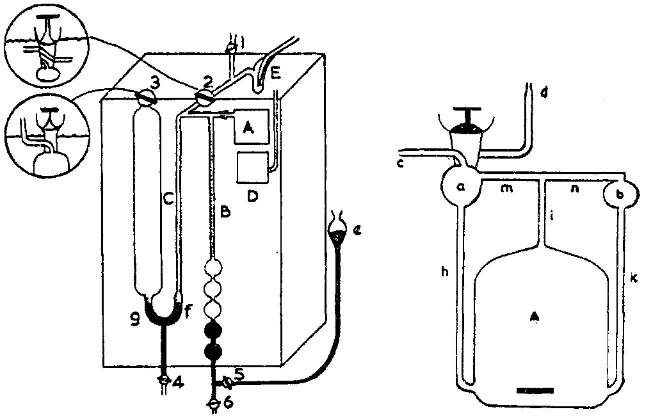

Figure 3.—The gas solubility apparatus of Ben-Naim and Baer (38). Reprinted from *The Transactions of the Faraday Society* by permission of the Faraday Society.

A microgasometric technique (originally developed by Scholander (544) whose paper should be read for details on microgasometric analysis) embodying some modifications of Steen's apparatus (581)was used by Douglas (152) to determine the solubility of oxygen, argon, and nitrogen in distilled water. This method takes advantage of the fact that the ratio of absorbed gas volume to liquid volume is constant at a given equilibrium pressure. Equilibration takes place within 30 min, small samples are used, and the estimated precision is ±0.25–0.50%. The temperature was regulated to ±0.01°. The procedure can be understood by referring to Figure 4. With G and D filled with mercury and H filled with water, degassed water is introduced into the side arm D with a 10-cc syringe and a blunt tipped needle. The plug E is replaced. With H half-filled with water and F filled with mercury to the top of the capillary, a conventional gas transfer pipet (filled with the pure gas) is seated on the capillary and the gas meniscus pulled down to the mark on the capillary. The micrometer is set (using the leveling bulb) to a zero reading and then some of the gas (using the micrometer) is pulled into the absorption chamber G. The water is removed from H except for an indicator drop in the capillary below H. When the system has equilibrated the gas volume is read. The gas-free water is tilted in from the side arm, mechanical shaking begun, and the indicator drop kept at its mark by adjusting the micrometer. When equilibrium is attained the final gas volume is read. Then by opening stopcock S-1 the liquid volume is read by screwing the micrometer in until the liquid level reaches the mark on the capillary. The procedure is said to be simple, precise and rapid. Another apparatus using small samples (5 cc) is described by Thomsen and Gjaldbaek (599).

Burrows and Preece (85) used a manometric method to determine the solubility of helium in three low-pressure oils. Their mixing chamber is shown in Figure 5. After the vessel J was charged with the degassed liquid it was charged with gas by draining liquid from J and weighing it. The stirrer moves the magnet-containing ring R (stirring the liquid in the thermostated bath) which moves the perforated steel disk (stirring the oil and gas in the mixing chamber). The temperature is varied in 20° intervals from 20 to 80°. The precision appears to be of the order of ±2%. Ridenour, *et al.* (501), used a manometric method to

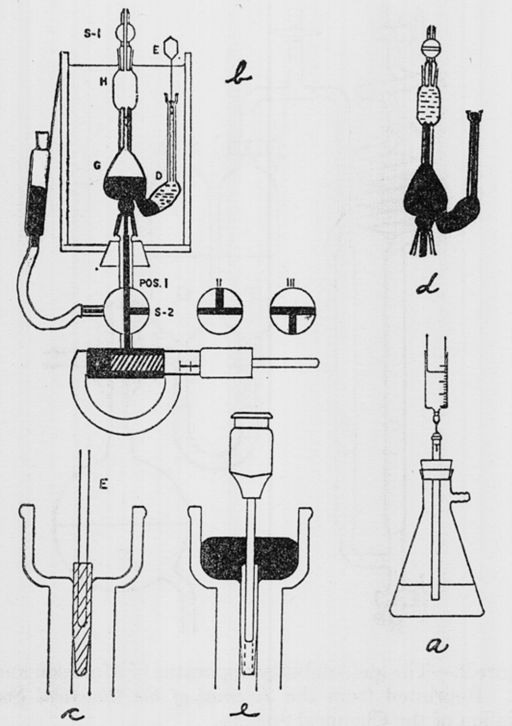

Figure 4.—The gas solubility apparatus of Douglas (152). Reprinted from *The Journal of Physical Chemistry* by permission of the copyright owners, The American Chemical Society.

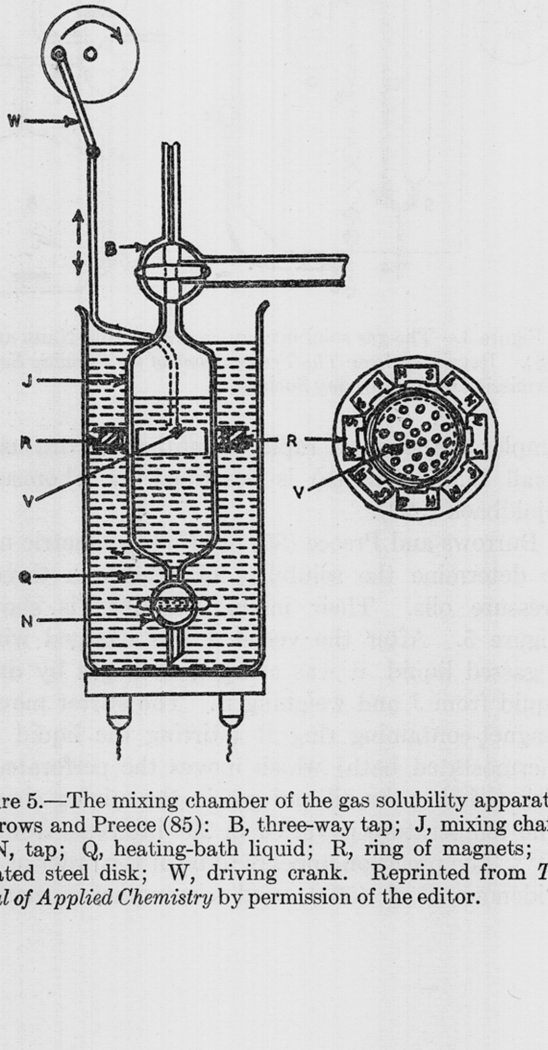

Figure 5.—The mixing chamber of the gas solubility apparatus of Burrows and Preece (85): B, three-way tap; J, mixing chamber; N, tap; Q, heating-bath liquid; R, ring of magnets; V, perforated steel disk; W, driving crank. Reprinted from *The Journal of Applied Chemistry* by permission of the editor.

determine gas solubilities (to about ±3%) in molten paraffin and microcrystalline waxes. Baldwin and Daniel (22) describe a method for the determination of gas solubility (to ±1%) which is particularly useful with viscous liquids. Yeh and Peterson's apparatus (667) was used for gas solubilities in liquids and they report their precision as ±0.5%.

Loprest (374) developed an apparatus for the rapid determination of the solubility of gases in liquids at various temperatures. The apparatus was designed for a precision of ±1% and it is possible to obtain solubility data over a wide temperature range and at several partial pressures of the gas with a single charging of the system. Solvent does not come into contact with mercury surfaces. Wheatland and Smith (642) describe a simple gasometric method for the determination of dissolved oxygen in water and saline water, and their method is precise to ±0.5%. Klots and Benson (318) give details for an apparatus for determining the solubility of N_2, O_2, and Ar in distilled water in the temperature range 2–27° and with an estimated accuracy approaching 0.1%.

Koonce and Kobayashi (330) designed an apparatus for the solubility of methane in *n*-decane for the pressure range 200–1000 psia and the temperature range of −20 to 40°F. They estimated their probable error as ±1.5%. Zampachova (674) also described a simple manometric method for determining the solubility of vapors in liquids at elevated pressures. Krichevskii and Sorina (337) give details for an apparatus for determining hydrogen solubility in cyclohexane in the temperature range 20–60° and up to 700 atm.

Cox and Head (114) described a novel apparatus for determining (to ±1%) the solubility of CO_2 in HF solutions. The solubility chamber was gold-plated. Karasz and Halsey (294) detail an apparatus for measuring the solubility of helium and neon in liquid argon over the temperature range 83.9–87.5°K, and with the general limits of error as 0.1%. The apparatus described by Kobatake and Hildebrand (322) was used for determining (to ±0.3% and the range 5–30°) the solubility of a large number of gases in various solvents. Swain and Thornton (592) describe an apparatus for measuring the solubility of the methyl halides in light and heavy water at 29 and 40°. The apparatus of Tsiklis and Svetlova (615) was used for the solubility of HCl, Cl_2, NOCl, NO, and H_2S in cyclohexane in the range 10–40°. Kogan and Kol'tsov (328) describe an apparatus precise to ±0.25% for the solubility of Cl_2 in CCl_4 in the range −20 to 71°. Bodor, *et al.* (54), describe an apparatus for determining gas absorption in liquids in the range −80 to 0°.

B. MASS SPECTROMETRIC METHODS

The mass spectrometer may be used for gas solubility determinations. Basically, the technique calls for outgassing a sample of a gas-saturated solvent, trapping the gas, and then analyzing the gas by mass spectrometry. Such equipment was described by Cseko (116–118) for the determination of the solubility of gases and gas mixtures in liquid ammonia. In this way he determined the solubility of argon in liquid ammonia at room temperature and the pressure range 20–100 atm. Cantone and Gurrieri (91) used mass spectrometry to analyze water samples for CH_4, O_2, N_2, and Ar. Faulconer and co-workers (177A, 241A, 469A, 479) describe mass spectrometric techniques for the analysis of various gases in blood.

A prime advantage of using the mass spectrometer as an analytical tool is the ability to determine the ratio of dissolved gases and isotope effects in dissolved gases. Benson and Parker (42) describe the technique they used for the determination of N_2/Ar and N_2/O_2 ratios in distilled water and sea water in some detail. The precison with which they determined these ratios was given as $\pm 1\%$. Of course, by using standard values for the solubility of any one of the gases in a pair, the solubility of the second gas may be determined. For a more accurate determination of the N_2/Ar ratio the extracted gas was cycled through a "Vycor" furnace at 700° filled with copper turnings. Benson and Parker (41) used the same basic technique, modified for collecting samples at sea, to determine N_2/Ar and nitrogen isotope ratios in aerobic sea water. Klots and Benson (319) determined the isotope effect in the solution of oxygen ($^{32}O_2$ and $^{34}O_2$) and nitrogen ($^{28}N_2$ and $^{29}N_2$) in distilled water in the temperature range 2–27°. They found the extrapolated values of the ratio of the Henry's law constants at 0° to be 1.00085 ± 0.00010 for nitrogen and 1.00080 ± 0.00015 for oxygen. Benson (42A) discusses applications of the mass spectrographically determined ratios to problems in oceanography.

C. GAS CHROMATOGRAPHIC METHODS

In gas–liquid partition chromatography (glpc) a liquid (normally high boiling) is supported in a column on an inert stationary phase. A carrier gas continually bathes the liquid, and one can assume an equilibrium exists between the passing carrier gas and the amount of this gas which has dissolved in the liquid. A third substance (vapor, gas, or a mixture) is transported in the carrier gas and is partitioned between the carrier gas stream and the stationary liquid phase. Partition coefficients are determinable from knowing the retention volumes and column characteristics. By also knowing the column dimensions and the quantity of partitioning liquid it is possible to determine gas solubilities. Of course, gas solubilities measured in this way are measured for systems under special constraints: (1) the liquids are restricted to high boilers; (2) the solubility is for a gas or vapor in a film of liquid (supported on a solid phase) and in which the carrier gas is already equilibrated; (3) the process involves steady states and transient equilibriums as the carried component is swept through the column; (4) in the portion of the gas stream where the carried component is, the carrier gas concentration is less than normal and as this portion of the gas stream passes any given point some of the carrier gas must be outgassed; and (5) it is difficult to ascertain the carried component partial pressure as it is swept along as a band which may or may not be symmetrical in its concentration distribution. Despite such difficulties Zorin, Ezheleva, and Devyatykh (685) were able to determine the soubility of CH_4, C_2H_2, C_3H_6, isobutane, isobutylene, and CO_2 in certain solvents, and their results were compared with static methods of determining solubility.

Of further significance is the fact that partition coefficients which are determinable from glpc are in a way gas solubilities, but the considerations mentioned in the last paragraph must be kept in mind. Two texts which give more details on determining partition coefficients (and other matters) are ref 124 and 80. Kurkchi and Iogansen (349) used glpc for determining the solubility of C_2H_2, C_3H_4, and C_4H_4 in several solvents and found that their results agreed within 5% with literature values. They describe their apparatus in detail.

The major use of gas chromatography in gas solubility determinations has been as an analytical tool for the quantification of gases extracted from saturated solutions of liquids. In this sense the gas chromatographic methods are similar to the mass spectrometric methods described in the last section. The advantage of gas chromatography as an analytical tool is the relative simplicity, low cost, and rapidity of the measurements. Reproducibility is of the order of 1–2%, but uncertainties in the extraction of the dissolved gas makes the over-all precison a bit poorer. Some unique extraction methods have been devised.

A particularly simple procedure was described by McAuliffe (400) who determined the solubility in water of C_1–C_9 hydrocarbons. A 0.05–0.10-cc sample of the hydrocarbon-saturated water was directly injected into a gas chromatograph fitted with a suitable fractionator containing a drying agent to absorb water, the released hydrocarbon passing directly into the chromatograph column. Hydrocarbon concentrations were determined by measuring areas under curves and comparing with calibrations arrived at by using known amounts of the pure hydrocarbons. The same author (401) used a similar technique to determine the solubilities in water of 65 (paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic) hydrocarbons. Swinnerton, Linnenbom, and Cheek (593) determined the amount of dissolved gases in aqueous solutions by stripping the

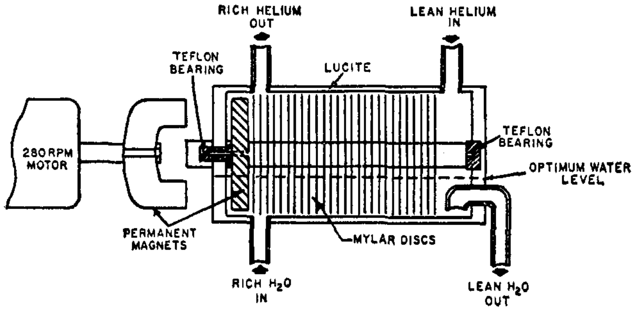

Figure 6.—Detail of the stripper used by Williams and Miller (652) to remove dissolved gases from a saturated liquid. Reprinted from *Analytical Chemistry* by permission of the copyright owners, The American Chemical Society.

gases from the solutions in an all-glass sample chamber which is divided into two parts by a coarse glass-fritted disk. A known quantity of the saturated liquid is admitted to the sample chamber through a rubber serum cap. The carrier gas coming up through the fritted glass disk in a stream of fine bubbles completely strips the solution of its dissolved gases quickly and effectively. The same authors (594) described an improvement of their sampling procedure. Elsey (167) describes a similar procedure for the determination of dissolved oxygen in lubricating oil. Wilson and Jay, *et al.* (656), used a fritted-glass sample chamber coupled with gas adsorption chromatography for the analysis of blood gases and found that their approach gave results of equal precision to the van Slyke technique. In a subsequent paper Jay and Wilson, *et al.* (278), utilized the same apparatus for determining absorption coefficients for nitrous oxide in distilled water and in whole blood. The gas chromatographic technique again gave results comparable to the van Slyke technique, but the former method has some advantages in speed, the ability to resolve gas mixtures readily, and overcoming the disadvantage found in the van Slyke method of having to make a correction for the small but variable amounts of gas which are not extracted.

The problem of stripping or extracting dissolved gas was solved by Williams and Miller (652) in an interesting way. Figure 6 shows the details for their device which is used for stripping on a continuous basis (the gas-saturated liquid flows countercurrent to the carrier gas which also serves as the inert stripping gas) with intermittent sampling and analysis by a commercial gas chromatographic unit. They compared several common techniques for purging water: dynamic and static vacuum, with and without manual and ultrasonic agitation; ultrasonic treatment alone; and purging with an inert gas (argon and helium). The most effective system tested was inert gas purging at flow rates of 500–1000 cc/min of 100-cc water samples. This technique removed 95–98% of the dissolved oxygen in 15–30 sec, where the next best technique of dynamic vacuum with agitation took 1–2 min to remove the same quantity of gas. In the gas chromatographic approach the rapidity of removal of dissolved gas is extremely important. The stripping unit (Figure 6) is about 4 in. long and 2 in. in diameter. As the mylar disks rotate through the liquid phase (kept at an optimum level of about one-fourth of the stripper volume), a thin film of liquid (which is being continuously renewed) is spread over their surfaces and exposed to the gas phase. The rate of gaseous exchange is very rapid. They found essentially 100% gas removal for helium/water ratios of 10:1 through 1:2 for up to 100 ml/min flow rates. Since it is necessary to have both accurate knowledge and control of the gas and water flow rates, a ratio of 1:1 was arbitrarily chosen for their work to simplify the calculations. This simple and efficient gas stripper should find wide use.

Ikels (266, 267) used a gas chromatographic technique to determine the solubility of nitrogen and neon in water and extracted human fat. Kruyer and Nobel (347) measured the solubility of hydrogen in five solvents by stripping the gas from the solvent and measuring areas under an expulsion curve. The method was said to be precise to ±3%.

D. CHEMICAL METHODS FOR DISSOLVED OXYGEN

Chemical methods have been long used for the determination of dissolved oxygen in pure water, natural waters, and aqueous solutions. In recent years there has been much controversy over oxygen solubilities in water, and this has sparked many new studies. The manometric approaches were discussed earlier, and most workers take the results of Klots and Benson (318) to be the most reliable.

The Winkler method (657) and modifications of it have been among the most popular and the most accurate. Briefly, the Winkler method involves the oxidation of freshly precipitated manganous hydroxide by the dissolved oxygen to form manganic hydroxide. This step is favored by high pH. The solution is then made acidic under which conditions the manganic ion oxidizes iodide. In the presence of excess iodide the iodine is largely present as the complex triodide. In the last step the iodine is titrated with thiosulfate which is oxidized to tetrathionate. Excess thiosulfate is back-titrated amperometrically with standard potassium iodate reagent. The equations for these steps are

$$\mathrm{Mn^{2+} + 2OH^- = Mn(OH)_2}$$

$$\mathrm{2Mn(OH)_2 + {}^1/_2O_2 + H_2O = 2Mn(OH)_3}$$

$$\mathrm{2Mn(OH)_3 + 6H^+ + 3I^- = 2Mn^{2+} + I_3^- + 6H_2O}$$

$$\mathrm{I_2 + I^- = I_3^-}$$

$$\mathrm{I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}}$$

The method depends on strict control of pH and iodide concentration. Possible errors in the Winkler method have been recently and extensively discussed (91A, 91B, 424).

The work of Truesdale, *et al.* (610), began the modern determinations of dissolved oxygen. They critically evaluated earlier work and made new measurements but, unfortunately, their work contains a systematic error and is low by some 2.5% Dr. B. A. Southgate, who is Director of Water Pollution Research at the Water Pollution Research Laboarory, Stevenage, Herts., England, believes that the true story is contained in ref 424, although both studies were carried out at his institution. In part, a private communication from Dr. Southgate states, "One thing which has come out of this work (424) is that it is pretty obvious that a very large proportion of the determinations of dissolved oxygen made before about 1961 or 2 must have been incorrect for the same reason that the solubility values determined by Truesdale (610) were incorrect. The biggest source of possible error of course occurs if one uses the present-day accurate values for solubility with incorrect determinations of concentration in water, and from these two values calculates the oxygen deficit."

The paper by Montgomery, Thom, and Cockburn (424) described their modification of the Winkler method, and with their improved procedure they determined the solubility of oxgyen in pure water (0.4–27°) and in sea water (2–27°). The agreement between their results and that for other workers (for solubilities in pure water) is shown in Figure 7. The ordinate in this figure is mg O_2/l., where the oxygen solubility expressed in this unit goes from 14.63 at 0° to 6.47 at 40°. They critically discuss earlier work, and in particular showed that the values of Truesdale, *et al.* (610), were low due to losses of iodine vapor. They found that the effect of initial concentration on the rate of loss of iodine outweighs that of initial temperature, so that the loss of iodine is greater for water samples saturated with oxygen at a low temperature than for those saturated at a high temperature. This conclusion was verified experimentally, although others (166, 231) and Truesdale, *et al.* (610), have speculated on the reasons for the "low" values.

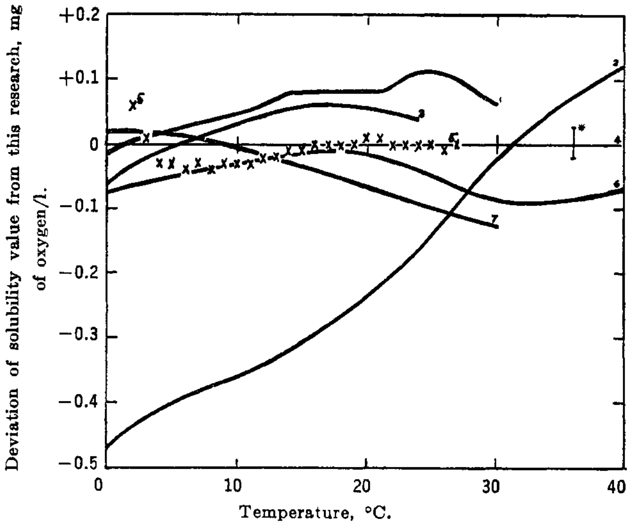

Figure 7.—Comparison of oxygen solubility values in pure water obtained by various authors with the values of Montgomery, *et al.* (424). (1) Whipple, G. B., and Whipple, M. C., *J. Am. Chem. Soc.*, **33,** 362 (1911); (2) Truesdale, *et al.* (610); (3) Carlson, T., *Akad. Afh. Stockholm,* 1912; (4) ref 424; (5) Klots and Benson (318); (6) Winkler (657); (7) Elmore and Hayes (166). * Root mean square deviation of the work in ref 424. Reprinted from *The Journal of Applied Chemistry* by permission of the editor.

A description of the Montgomery, *et al.*, procedure follows. The sample is collected by standard techniques in a 65-cc bottle with a well-fitting ground-glass stopper. Without delay, 0.4 ml of manganous sulfate solution (480 g $MnSO_4 \cdot 4H_2O$/l.) is added below the surface, followed by 0.4 cc of alkaline iodine solution added at the surface. (The alkaline iodide solution is prepared according to the method of Pomeroy and Kirschman.) The bottle is stoppered so as to exclude air bubbles and shaken by rapidly inverting 12–15 times. After the precipitate has settled to the lower third of the bottle, it is shaken again (essential) and allowed to settle completely. Sulfuric acid (1 cc of a solution containing 400 cc of the concentrated acid per liter) is added down the neck of the bottle, which is restoppered (excluding air bubbles) and the contents mixed by shaking. After 10 min an aliquot is removed by pipet and titrated without delay with 0.0025 *N* thiosulfate solution. The thiosulfate is standardized against an iodine solution which is prepared by adding 20.00 ml of 0.0025 *N* potassium iodate solution to a few milliliters of water containing a quantity of alkaline iodide reagent equivalent to that present in sample titrations. Iodine is liberated by addition of the appropriate quantity of 40% sulfuric acid, which must be mixed thoroughly with alkaline solution before titration is begun, or too high a factor will be obtained. The calculated concentration of dissolved oxygen is multiplied by 1.012 to allow for dilution by the manganous sulfate and alkaline iodide reagents. The end point of the titration is determined amperometrically. Apparently, one of the important factors in these chemical methods is technique, and some practice is required. Tables IV and V in Montgomery, *et al.*, provide some interesting comparisons. The first table compares the results of their procedure with five others (showing excellent agreement with Elmore and Hayes (166)). The second table shows the effect of speed of manipulation and titration in standard modifications of the Winkler method. The work of Montgomery, *et al.*, deserves careful study.

Elmore and Hayes (166) undertook an independent check of the solubility of oxygen in water. They carried out some 260 determinations in 52 replicate groups of experiments in the range 1.8–29.3°. The standard deviation in the measurements is of the order of 0.2%, and the results are presented in a table from 0–30° in

0.1° intervals. They followed a modification of the Winkler method using an amperometric end point. This paper critically evaluates earlier work and they conclude that their values are "the most satisfactory of those presently available for application to natural stream conditions."

Morris, Stumm, and Galal (425) determined the solubility of oxygen in water by both manometric (11–30° and a precision of about 0.5%) and chemical (5–29° and a precision of about 0.3%) methods. Their work is in good agreement with the best recent measurements. They suggest that a possible reason for the results of Elmore and Hayes being slightly low at 30° is that they may have omitted making the temperature correction for a mercury barometer. This amounts to a negative correction of about 0.4% at 25°.

The most recent determination of oxygen solubilities in pure water and sea water has been that of Green (231) in the range 0–35°. This independent work is in excellent agreement with Klots and Benson (318) and with Montgomery, *et al.* (424). The error in this work is estimated at ±0.27%. Green's thesis contains an excellent analysis of earlier work and sources of error in the Winkler method, a modification of which he used.

It is gratifying to note the excellent agreement among recent workers, and it appears that with this agreement and the attendant explanations of earlier discrepancies that a truly definitive set of values for the solubility of oxygen in water has been attained.

Wheatland and Smith (642) used both a gasometric method and the Winkler method and found that their results from the two approaches agreed within experimental error (about 0.2%). Czerski and Czaplinski (123) determined the solubility of oxygen in air-saturated liquids by stripping the liquids with a carrier gas and then passing this through an electrochemical detector. The probable error is estimated at 0.9 mg O_2/l.

E. MISCELLANEOUS METHODS

Enns, Scholander, and Bradstreet (169) give details of a method they used for the determination of the solubility of O_2, N_2, Ar, He, and CO_2 in water and sea water at hydrostatic pressures up to 102 atm. For all gases examined the equilibrium pressure increased about 14% per increase in hydrostatic pressure of about 100 atm. The method also permits the calculation of partial molal volumes of the dissolved gases. Buell and Eldridge (79) describe an apparatus for gas solubility at high pressures where glass systems cannot be used. Khiteev (309) describes a mercury-free, high-pressure solubility apparatus for gases in petroleum. Safronova and Zhuze (518) also describe an apparatus for high-pressure, high-temperature solubilities in crude oils. Miner's apparatus (421) was constructed for measurement of the solubility of O_2 and N_2 in liquid CO_2 at pressures up to 1000 atm and in the range −40 to 32°. At the low-temperature end Denton, Lucero, and Roellig (143) describe an apparatus for the solubility of He in liquid hydrogen. The apparatus of Hu and MacWood (265) was designed for determining the solubility of gases in liquids at 113–181°K and 0–40 atm.

An apparatus for the solubility of He, Ne, Ar, and Xe in molten fluorides at 0.5–2 atm and 600–800° is described by Grimes, Smith, and Watson (232). The molten fluoride is first saturated with a gas. Then the dissolved gas (in a known volume of the molten fluoride) is stripped with a second inert gas and the sample collected and analyzed on a mass spectrometer. Ryabukhin (511) gives details for an apparatus for determining the solubility of Cl_2 in fused chlorides at 700–1050°.

The most commonly used method for gas solubilities in molten materials is Sievert's method. This is basically a gas-handling method where the total number of moles of gas introduced into the system is determined by measuring *P*, *V*, and *T;* and then by measuring the equilibrium pressures in the calibrated system the quantity of absorbed gas may be calculated. This approach is also used for gas–solid absorption determinations. Gas extraction methods are also employed. Some recent papers describing apparatus for gas solubilities in molten metals are ref 537 and 472. Mulfinger and Scholze (435) describe an apparatus for solubility in molten glasses.

Bar-Eli and Klein (28) describe a method for determining gas solubility by measuring the rate of reaction between a gas and its solvent. This method should prove useful in those systems where the gas reacts with the solvent. Alexander (10) describes a microcalorimeter which he used to directly determine heats of solution of Ne, Ar, Kr, and Xe in water.

Other papers which give details on gas solubility apparatus are: ref 480—NO in aqueous solutions; ref 38—SO_2 in aqueous ammonia solutions; ref 470—CH_2CHCl in methanol and trichloroethylene; ref 239, 512, 616—C_2H_2 solubility in various solvents; ref 234—solubility in waxes in the range 200–400°.

In general, most of the papers on the solubility of gases in liquids give detailed descriptions of the procedure. The gas solubility tables can serve as a general guide for references to apparatus applicable to particular problems.

IV. METHODS OF EXPRESSING GAS SOLUBILITY

Gas solubilities have been expressed in a great many ways. The more popular of these along with interconversion formulas are presented. Since there are so many methods of expressing solubility, it is extremely important that each paper present a careful exposition of the manner in which their solubilities were calculated and to also include a sample calculation to be doubly certain. This was emphasized by Markham and Kobe (393) but bears repetition along with repeating much of what they said about definitions.

A. THE BUNSEN COEFFICIENT, α

The Bunsen coefficient, α, is defined as the volume of gas, reduced to 0° and 760 mm pressure of mercury, which is absorbed by the unit volume of solvent (at the temperature of the measurement) under a gas pressure of 760 mm. When the partial pressure of the gas above the solvent differs from 760 mm, it is corrected to this pressure by Henry's law. By way of example an equation which can be used to calculate the Bunsen coefficient is

$$\alpha = \left[\left(V_g \frac{273.15}{T} \frac{P_g}{760}\right)\left(\frac{1}{V_s}\right)\right]\left(\frac{760}{P_g}\right) \quad \text{(Eq 1)}$$

where P_g is the partial pressure (in mm Hg) of the gas above the solution, T is the absolute temperature, V_g is the volume of gas absorbed (at T and the total pressure of the measurement), and V_s is the volume of the absorbing solvent. If the solvent has a nonnegligible vapor pressure, then $P_g = P_T - P_s$ where P_T is the total pressure in the system and P_s is the solvent vapor pressure. Equation 1 obviously reduces to

$$\alpha = \frac{V_g}{V_s} \frac{273.15}{T} \quad \text{(Eq 2)}$$

The corrections to standard conditions assume ideal gas behavior. Since real gases do not follow the ideal gas law, it is extremely important to specify the gas equation of state used for the correction to standard conditions. For most gases and conditions the difference is negligible, being less than 1%, but the method of correction should still be specified. The Bunsen coefficient is sometimes just referred to as the absorption coefficient or the coefficient of absorption.

The Kuenen coefficient, S, is the volume of gas (in cubic centimeters) at a partial pressure of 760 mm reduced to 0° and 760 mm, dissolved by the quantity of solution containing 1 g of solvent. Thus the Kuenen coefficient is proportional to gas molality.

B. THE OSTWALD COEFFICIENT, L

The Ostwald coefficient, L, is defined as the ratio of the volume of gas absorbed to the volume of the absorbing liquid, all measured at the same temperature. The Ostwald coefficient is then

$$L = V_g/V_s \quad \text{(Eq 3)}$$

For the reaction Gas (in liquid phase; C_l) = Gas (in gas phase; C_g), the Ostwald coefficient may be written as

$$L = \frac{C_l}{C_g} = \frac{V_g}{V_s} \quad \text{(Eq 4)}$$

where C_l is the concentration of the gas in the liquid phase and C_g is the concentration of the gas in the gas phase. The Ostwald coefficient is in reality an equilibrium constant, and as such is independent of the partial pressure of the gas as long as ideality may be assumed. However, to fix the value of the Ostwald coefficient, the temperature and the total pressure must be designated.

If the total pressure is kept at 760 mm, then the volume of gas absorbed, reduced to 0° and 760 mm by the ideal gas laws, per unit volume of liquid is frequently designated as β, an absorption coefficient. It is important to clearly specify the method of calculating the solubility since β sometimes gets confused with α.

C. THE HENRY'S LAW CONSTANT

The equation for a gas in equilibrium with a liquid may be written as Gas (in liquid phase; X_l or C_l) = Gas (in gas phase; P_g or C_g).
Henry's law can then be presented as

$$P_g = K_1X_l \quad \text{(Eq 5)}$$

or in the case of a dilute solution of the gas as

$$P_g = K_2C_l \quad \text{(Eq 6)}$$

$$C_g = K_cC_l \quad \text{(Eq 7)}$$

From the last equation it is noted that $L = 1/K_c$. In the above equations X is the mole fraction and, of course, solubility may be expressed in terms of mole fractions. The volume fraction, molarity, and molality can also be used to express solubility.

The Henry's law constants, particularly K_2, can be satisfactorily used to express solubility, but it must be remembered from thermodynamics that Henry's law is applicable only over a restricted range for dilute solutions and that Henry's law in practice is frequently just a limiting law. The method of calculating the Henry's law constant must be specified. The practice of converting solubility data from the experimental pressure to a partial gas pressure of 760 mm by applying Henry's law usually introduces no errors if the pressure range is reasonably small.

D. THE WEIGHT SOLUBILITY, C_w

The weight solubility, C_w, is recommended by Cook (103) as a more logical unit than either the Bunsen or Ostwald coefficients. C_w is defined as the number of moles of gas, with the partial pressure of the gas being 760 mm, per gram of solvent. This unit has the advantage of essentially being a ratio of weights, thus permitting easy conversions and making certain calculations simpler.

E. INTERCONVERSION OF THE SOLUBILITY EXPRESSIONS

(a) From the Bunsen coefficient

$$\beta = \alpha(760 - P_s)/760 \quad \text{(Eq 8)}$$

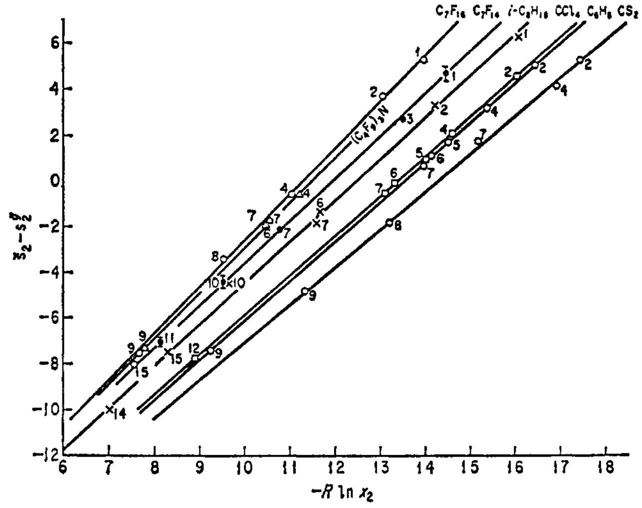

Figure 8.—Entropy of solution of gases. 1, He; 2, H_2; 3, Ne; 4, N_2; 5, CO; 6, O_2; 7, Ar; 8, CH_4; 9, CO_2; 10, Kr; 11, Xe; 12, C_2H_2; 13, C_2H_4; 14, C_2H_6; 15, SF_6. Reprinted from "Regular Solutions" (244) by permission of the authors and the copyright owners, Prentice-Hall, Inc., Englewood Cliffs, N. J.

$$L = \alpha(T/273.15) = \beta(T/273.15)(760)/(760 - P_s) \qquad \text{(Eq 9)}$$

$$S = \frac{\alpha}{\rho_s(1 - u)} \qquad \text{(Eq 10)}$$

$$C_w = \alpha/V_0\rho \qquad \text{(Eq 11)}$$

P_s is the partial pressure of the solvent, ρ_s is the density of the solution, u is the decimal fraction of solute in solution, V_0 is the molal volume of the gas in cc/mole at 0°, and ρ is the density of the solvent at the temperature of the measurement.

$$K_1 = \frac{17.033 \times 10^6\rho_s}{\alpha M_s} + 760 \qquad \text{(Eq 12)}$$

$$K_2 = 17{,}033/\alpha = \frac{22{,}414 \times 760}{1000\alpha} \qquad \text{(Eq 13)}$$

M_s is the molecular weight of the solvent. The units of K_1 are those of pressure (mm Hg), and only for the very soluble gases does the constant term of 760 mm alter significantly the value of K_1 calculated from the first term in Eq 12. The units of K_2 are (mm Hg)(liters of solvent)/mole of gas.

(b) From the Ostwald coefficient

$$\alpha = L(273.15/T) \qquad \text{(Eq 14)}$$

$$\beta = L(273.15/T)(760 - P_s)/760 \qquad \text{(Eq 15)}$$

$$K_c = 1/L \qquad \text{(Eq 16)}$$

$$C_w = L/V_t\rho \qquad \text{(Eq 17)}$$

V_t is the molal volume of the gas in cc/mole at the temperature of the measurement.

(c) From the Henry's law constant, K_1

$$\alpha = \frac{17.033 \times 10^6\rho}{(K_1 - 760)M_s} \qquad \text{(Eq 18)}$$

The 760 mm in the denominator may be neglected unless it is appreciable with respect to K_1.

(d) From the weight solubility, C_w

$$X = C_wM_s/(1 + C_wM_s) \qquad \text{(Eq 19)}$$

V. SOLUBILITY THEORY AND RELATIONSHIPS

A. GAS SOLUBILITY AND THEORIES OF SOLUTION

1. *Regular Solution Theory*

Regular solution theory has been most consistently applied to gas solubilities by Hildebrand and coworkers. The two books by Hildebrand and Scott (243, 244) contain excellent individual chapters on gas solubilities, namely, Chapter XV in ref 243 and Chapter IV in ref 244. Hildebrand and Scott (243, p 4) define regular solutions with the following sentence: "A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged."

There are two equations based on regular solution theory frequently used to calculate gas solubilities. The first is

$$-\log X_2 = -\log X_2^{\mathrm{i}} + \frac{0.4343\bar{V}_2}{RT}(\delta_1 - \delta_2)^2 \qquad \text{(Eq 20)}$$

In this equation X_2 is the mole fraction gas solubility, X_2^{i} is the ideal gas solubility (calculable from Raoult's law), $\bar{V}_2$ is the partial molal volume of the gas in the solution, and the δ's are solubility parameters where the subscript 1 refers to the solvent. The solubility parameter, δ, sometimes referred to as the cohesive energy density, is the square root of the energy of vaporization per cc or $\delta = (\Delta E^{\mathrm{V}}/\bar{V})^{1/2}$, where ΔE^{V} is the molar energy of vaporization and $\bar{V}$ is the molar volume. For solutions where the molecules differ in size (Flory–Huggins model) the following equation is used

$$-\log \phi_2 = -\log X_2^{\mathrm{i}} + 0.4343\left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right)\phi_1 + \frac{0.4343\bar{V}_2\phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad \text{(Eq 21)}$$

where ϕ is the volume fraction and $\bar{V}_1$ is the molar volume of the solvent. Upon introducing some simplifying approximations the previous equation becomes

$$-\log X_2 = -\log X_2^{\mathrm{i}} + \log\frac{\bar{V}_2}{\bar{V}_1} + 0.4343\left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right) + \frac{0.4343\bar{V}_2}{RT}(\delta_1 - \delta_2)^2 \qquad \text{(Eq 22)}$$

For gases above their critical temperature the terms X_2^{i}, δ_2, and $\bar{V}_2$ are evaluated by various extrapolations and approximations. Gjaldbaek and Hildebrand (219) in a paper on the solubility of chlorine in n-perfluoroheptane and other liquids justified the substitution of the partial molal volume of the gas in the solution for for molal volume of the pure gas. Despite the many assumptions made in the derivation of Eq 20, 21, and 22 they have proved to be remarkably satisfactory for solutions where both solvent and solute are nonpolar, and have been shown to give a fair approximation for slightly polar solvents. In some cases experimentally determined gas solubilities have been used in conjunction with the above equations to arrive at empirical values for the gas solubility parameters. Among others Clever, *et al.* (97), have done this and also applied regular solution theory to rare gas solubilities (95–98). Three recent papers by Thomsen and Gjaldbaek (599–601) have compared calculated with experimental solubilities for a variety of gases in a variety of solvents. In ref 600 they show an interesting correlation (a straight line) between δ_2 calculated empirically from solubility measurements and δ_2 calculated from $[(\Delta H^V - RT)/\bar{V}]^{1/2}$ where ΔH^V is the heat of vaporization. Gjaldbaek and co-workers in a series of papers (216–223, 358), which are most useful and interesting for the range of systems investigated and the reliability of the measurements, have supplied the most extensive testing of Eq 20, 21, and 22. Gjaldbaek and Anderson (221) included an additional term in Eq 20 to account for the dipole contribution to the energy of vaporization for polar solvents.

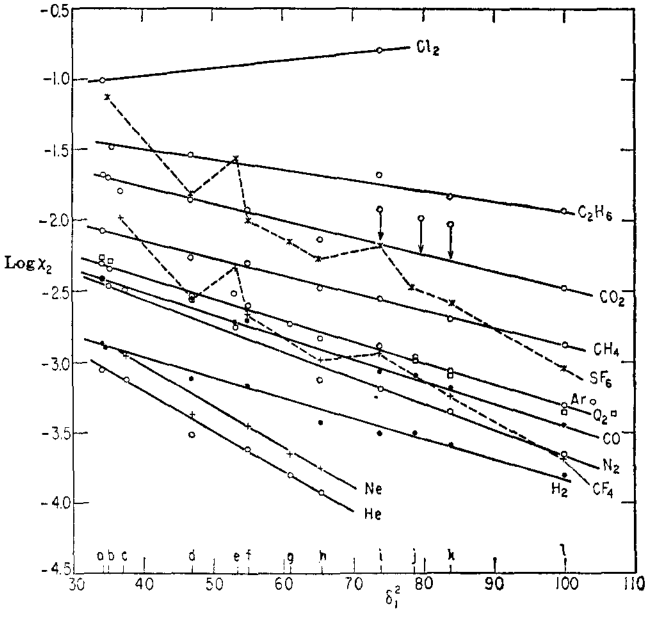

Figure 9.—Gas solubilities at 25° and 1 atm in log X_2 *vs.* the square of the solubility parameters of the solvents, δ_1: (a) C_7F_{16}, (b) $(C_4F_9)_3N$, (c) c-$C_6F_{11}CF_3$, (d) i-C_8H_{18}, (e) $CCl_2F \cdot CClF_2$, (f) n-C_7H_{16}, (g) $C_6H_{11}CH_3$, (h) c-C_6H_{12}, (i) CCl_4, (j) $C_6H_5CH_3$, (k) C_6H_6, (l) CS_2. Unpublished results reprinted by special permission of the author, Professor Joel H. Hildebrand.

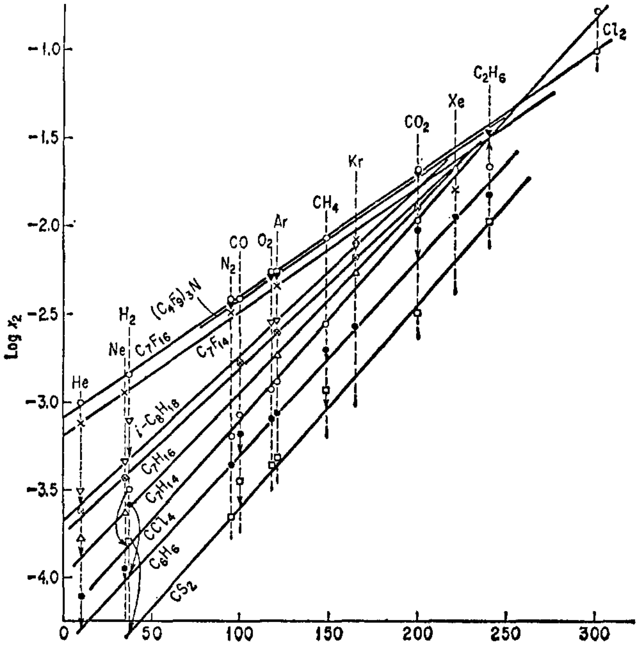

Figure 10.—Solubility *vs.* "force constant" of gases. Reprinted from "Regular Solutions" (244) by permission of the authors and the copyright owners, Prentice-Hall, Inc., Englewood Cliffs, N. J.

Jolley and Hildebrand (282) critically reviewed the literature for reliable gas solubilities which suited their purpose and drew a number of conclusions which are quoted below and illustrated in Figures 8, 9, and 10 taken from ref 244: "(a) For a given series of gases at 1 atm and 25° dissolving in a series of solvents, log X_2 decreases with increasing solubility parameter, δ_1, of the solvent. (b) For different gases in the same solvent, log X_2 increases linearly with increasing Lennard-Jones force constant, ϵ/k, of the gas. (c) The entropies of solution of different gases in the same solvent vary linearly with R ln X_2, and extrapolate at $X_2 = 1$ to the entropy of condensing to pure liquid the vapor of the solvent from a hypothetical pressure of 1 atm. The temperature coefficient of solubility may thus be obtained from its isothermal value. Solubility increases with temperature from common solvents when X_2 is less than about 10^{-3}, and *vice versa.* (d) The partial molal entropy of solution of any one gas from 1 atm to the same mole fraction (here 10^{-4}) is nearly the same in all solvents except fluorocarbons, where it is a little greater. In any one solvent, it increases in going to gases with smaller force constant. This is attributed mainly to increase in freedom of motion of the adjacent molecules of the solvent rather than to change in the behavior of the gas molecule in a 'cage'." Kobatake and Hildebrand (322) added data for many more systems, and Archer and Hildebrand (15) added data on the solubility of CF_4 and SF_6 in nonpolar solvents to the "regular" solutions.

Prausnitz (483) applied regular solution theory to gas–liquid solutions. He considered a three-step process: (a) isothermal compression of the pure gas from its partial pressure and the pure liquid from its vapor pressure to the isometric mixing pressure; (b) isothermal, isometric, and isopiestic mixing at the isometric mixing pressure; and (c) isothermal expansion of the solution from the isometric mixing pressure to the equilibrium pressure. The resulting equations gave reasonable estimates of the solubilities of gases and also of the temperature coefficient of solubility. Prausnitz and Shair (485) presented a thermodynamic correlation for gas solubilities based on the two-step process of condensing the gas isothermally to a hypothetical liquid at 1 atm and then dissolving this hypothetical liquid in the solvent. This paper contains much useful information including a semiempirical method for correlating the solubilities of gases in polar solvents. Sherwood and Prausnitz (566) derived a relationship for the accurate determination of heats of solution of gases at high pressure. Yen and McKetta (670) derived equations based on regular solution theory for the thermodynamic correlation of nonpolar gas solubilities in polar, nonassociated liquids. They were able to semiempirically correlate solubilities of nonpolar gases in both polar and nonpolar solvents. Lachowicz and Weale (353) also derived equations based on regular solution theory to predict gas solubility in nonpolar liquids, and their application of their equations to existing data resulted in useful correlations. Smith and Walkley (577) found that it was in general impossible to obtain solubility parameters for gases that lead to acceptable values for both the partial molal volumes and the solubility.

2. *Cell Potential and Cavity Models*

Uhlig (620) proposed a cavity model in which he considered the solubility process to take place in two steps: first, doing work on the solvent against the solvent surface tension to create a cavity, and, second, placing the gas molecule in this cavity and calculating the energy of interaction between the gas and solvent molecules. This is a simple theory but its prediction of a linear relationship between log L and the solvent surface tension has been borne out by many examples. Eley (161, 162) considered a two-step process similar to that of Uhlig's, but was able to more carefully evaluate the separate contributions of each step to the energy and the entropy changes involved. His approach showed reasonable success with both water and organic solvents, although he shows that the case of water is more complicated due to the possibility of structural modifications.

Reiss, *et al.* (496), extending ideas previously applied to the statistical mechanical theory of hard-sphere fluids determined an expression for the work of creating a spherical cavity in a real fluid. Systems such as helium in benzene are sufficiently close to the model to permit an experimental test of the theoretical expression, since Henry's law constants may be obtained from the expression. In addition, the surface tension and the normal heats of vaporization of fluids may be evaluated, and the authors found satisfactory agreement between calculated and experimental properties.

Pierotti (474) developed a method, using equations derived by Reiss, *et al.* (496), for calculating the reversible work required to introduce a hard sphere into a fluid and for predicting the solubility, the heat of solution, and the partial molar volume of simple gases in nonpolar solvents. The equations are derived for the two-step process of creating a cavity in the solvent of suitable size to accommodate the solute molecule (the reversible work or partial molar Gibbs free energy required to do this being identical with that for introducing a hard sphere of the same radius as the cavity into the solution), and then introducing into the cavity a solute molecule which interacts with the solvent according to some potential law, for instance, a Lennard-Jones (6–12) pairwise potential (the reversible work in the second step being identical with that of charging the hard sphere or cavity introduced in the first step to the required potential). By plotting the Henry's law constant against the polarizability of the solute gases for experimental data and extrapolating to zero polarizability a hard-sphere solubility is obtained which can be compared with solubilities calculated from the theory. This was done for He, Ne, Ar, Kr, N_2, H_2, and CH_4 in benzene and carbon tetrachloride at 298°K, and He, Ne, H_2, and D_2 in argon at 87°K; in all but one case the predicted solubility is well within a factor of 2 of the observed solubility, which is very good agreement considering the crude method used to obtain the interaction energy. By plotting the collision diameters of the rare gases against their polarizabilities and extrapolating to zero polarizability a hard-sphere diameter (2.58 A) corresponding to the extrapolated hard-sphere Henry's law constant may be evaluated. The theory also yields heats of solutions and partial molal volumes of the gases in solution. The predicted heats were usually within experimental error for all solutes except methane. The agreement between the predicted and calculated partial molal volumes is good, being better than those calculated by Smith and Walkley (577).

In a second paper (475) Pierotti developed a theory of gas solubility in water along lines similar to the earlier paper except for the introduction of a term involving the solvent dipole moment. Good agreement was found between the experimental and calculated heats, entropies, and molar heat capacities of solution, and for the partial molar volumes of the solutes. The calculated and experimental Henry's law constants for 16 solutes in water at 25° show good agreement, in only one case being off by a factor of 2. The "abnormal" thermodynamic properties of aqueous solutions were discussed with respect to the enthalpy and entropy of cavity formation. The theory is promising as a method for the investigation of gas solubilities in molten salts and molten metals. The thermodynamic properties of gas solubility in water and organic solvents were explained by one theory which involved no assumptions concerning the structure of the solvent.

Kobatake and Alder (323) discuss cell potentials and gas solubility theory. They develop a two-parameter cell potential in a free-volume-type theory which is determined from two experimentally obtained thermodynamic quantities. The cell potential for a gas dissolved in a liquid yields values of the free volume of the gas molecule that are about ten times larger than in a typical liquid. These large free volumes make the calculations less sensitive to the assumptions of the geometric arrangements of the neighboring particles and less dependent on the uncertainties in the knowledge of the intermolecular cell potentials. The large free volume indicates, as a number of authors have pointed out, that the gas molecule almost digs a "hole" in the liquid. Kobatake and Alder use this idea to calculate a reasonable value for the interfacial tension of carbon tetrachloride. For CH_4, N_2, Ar, O_2, and C_2H_6 in CCl_4 it was found that the gas molecule is surrounded by about seven neighbors and that the solvent molecules surrounding the gas contribute importantly to the thermodynamic functions. Further, it was found that the gas molecules perturb the solvent significantly over several molecular layers, while this is not the case in dilute liquid mixtures.

3. *Other Contributions to Theory*

Ridenour, *et al.* (501), derived an equation from a thermodynamic consideration of gas solubility as a special case of vapor–liquid equilibrium in which the system temperature may be higher than the critical temperature of the more volatile component of the mixture. The equation was applied with reasonable success to the solubility of CO_2, Ar, O_2, and N_2 in paraffin wax and the solubility of air in kerosene. Klots and Benson (320) discuss the thermodynamic properties of the atmospheric gases in aqueous solutions. Mastrangelo (398) derived an equation by statistical methods using a "quasi-chemical" type of equation for a two-component system that possesses one or more similar interactions per molecule. The agreement between the equation and data on the solubility of chlorofluoromethanes and ethanes in tetraethylene glycol dimethyl ether and chloroform in acetone was good. The equation should prove especially useful for solubility in polymeric solvents.

Himmelblau (247) uses a five-parameter equation for expressing the solubility of O_2, N_2, He, H_2, Xe, and CH_4 in water from the freezing point of water to near its critical point. The average deviation between the calculated and experimental Henry's law constants is about 3%. The partial molal heats and entropies of solution are presented from the freezing point to near the critical point of water. These partial molal heats of solution appeared to correlate linearly best at 25° with the force constants of the gases, and at 4° with the polarizability of the gases. Himmelblau and Arends (250) used the same five-parameter equation to correlate the solubility of O_2, N_2, H_2, He, Xe, CH_4, C_2H_4, C_2H_6, C_3H_8, n-C_4H_{10}, and 1-butene in water at high temperatures and pressures. Namiot (437) discusses the solubility under pressure of gases in water. In a paper on the solubility of nonpolar gases (He, H_2, Ar, Kr, Xe, CH_4, C_2H_6, C_3H_8) in water Namiot (439) derives an equation for calculating the number of water molecules bonded to one gas molecule, and also the number of displaced water molecules. These values were calculated for the above-mentioned gases. Amirkhanov (12) derived an equation for the theoretical calculation of the solubility in water of gases obeying Henry's law. The derivation assumes Maxwell's law of the distribution of molecular velocities and considers the thermal energy of the gaseous molecule, under equilibrium conditions. Using this equation the calculated solubility of Ne, Ar, Kr, and Xe was found to agree within experimental error with the experimental solubility.

Salvetti and Trevissoi (522) examined on the basis of irreversible thermodynamics the absorption of gases by liquids. Trevissoi and Ferraiolo (605) on a similar basis studied the absorption of gases by liquids considering the effect of surface tension.

4. *Special Studies*

The reasonably well-defined gaseous standard state and the low solubility of gases in liquids has attracted many workers to make studies in which the solubility of a gas is used as a "probe" to the understanding of a solvent property or to a gas–solvent molecular interaction. The extensive studies of the effect of an electrolyte solution on a nonelectrolyte activity is discussed in the section on salt effects. Several other studies are worth special mention.

Marvel, Copley, Zellhoefer, and co-workers (106–111, 677, 678) carried out an extensive study of hydrogen bonding. They determined the solubility of vapors of $CHCl_3$, CH_2Cl_2, CH_3Cl, CH_2ClF, $CHCl_2F$, $CHClF_2$, CCl_3F, CCl_2F_2, $C_2Cl_3F_3$, and $C_2Cl_2F_4$ in several hundred oxygen-containing compounds including alcohols, aldehydes, ketones, acids, ethers, and oximes as well as compounds containing nitrogen and sulfur functional groups. They concluded that the C–H group in the halocarbons can hydrogen bond and that ethers, aldehydes, ketones, and trialkylamines being the best solvents form the strongest hydrogen bonds.

The solubility of an acidic or basic gas can be correlated with the basicity of the solvent. Brown, *et al.* (75–77), used the solubility of HCl as a measure of the basic properties of aromatic nuclei.

Gerrard, Macklen, and co-workers have used hydrohalide gas solubilities (202–205, 207–212) as a measure of the basic function of oxygen and more recently sulfur (196) in certain organic functional groups. There is a detailed review of most of their work (206).

B. TEMPERATURE COEFFICIENT OF GAS SOLUBILITY

Only one direct calorimetric study of the heats of solution of gases has been made (10). All other values of the heat of solution of a gas in a liquid were derived from phase-equilibrium data *via* the important temperature coefficient of gas solubility. Progress is continuing to be made on understanding the basis of the temperature coefficient of solubility; however, useful predictions of the sign and magnitude of the temperature coefficient of solubility in all systems awaits a better understanding of intermolecular forces.

The rare gases are good examples of the types of gas solubility temperature dependence one observes. All the noble gases have a negative temperature coefficient of solubility in water around room temperature and atmospheric pressure which goes through a minimum and becomes positive at high temperatures and pressures. In hydrocarbon solvents at room temperature and atmospheric pressure helium and neon solubility increases with temperature, argon solubility is almost independent of temperature, and krypton and xenon solubilities decrease with temperature. In the molten salts studied to date all the rare gases have a positive temperature coefficient of solubility at temperatures between 600 and 900° and pressures ranging from 0.5 to 2 atm.

For gases dissolved in nonpolar solvents Hildebrand and co-workers have done much to bring order and understanding to the problem of the temperature dependence of solubility. Their work is well summarized in Chapter 4 of Hildebrand and Scott (244) where it is pointed out that for a sparingly soluble gas that obeys Henry's law the entropy of solution is

$$\bar{S}_2 - S_2^{\mathrm{g}} = R\left(\frac{\partial \ln X_2}{\partial \ln T}\right)_{\mathrm{sat}\ P} \qquad \text{(Eq 23)}$$

where X_2 is the mole fraction solubility. Experimentally it is observed that plots of log X_2 against log T are essentially linear for gases dissolved in nonpolar liquids. Thus, there is a regular system of relationships which exists between entropy and solubility with the dividing line between positive and negative temperature coefficient of solubility coming at $\bar{S}_2 - S_2^{\mathrm{g}} = 0$. Plots of $\bar{S}_2 - S_2^{\mathrm{g}}$ against $-R \ln X_2$ are linear for a series of gases in a given solvent (Figure 8). Gases with solubility less than about 10^{-3} mole fraction generally have positive temperature coefficient of solubility; gases with greater than about 10^{-3} mole fraction generally have negative temperature coefficients.

Hildebrand (244) has calculated the entropy of transferring gas at 1 atm to solution at 10^{-4} mole fraction for solvents varying from 5.8 to 10.0 in solubility parameter and gases varying from 10 to 300 in "force constants." The entropy increases moderately with decrease in solubility parameter and increases largely with decrease in force constant. Plots of the logarithm of mole fraction solubility against solvent solubility parameter squared show a smooth near-linear relation for each gas. Plots of the logarithm of mole fraction solubility against the gas "force constants" are linear for each solvent tested (Figures 9 and 10). Hildebrand shows that, excepting cases of specific interaction, the entropy of solution is the sum of two factors: dilution and expansion. These factors are both determined by the interrelations of intermolecular forces as measured by solvent solubility parameters and gas "force constants."

The temperature dependence of solubility has been used more often to get the heat of solution rather than the entropy of solution. Plots of log X_2 against $1/T$ are usually linear to the accuracy with which gas solubility is commonly measured. A temperature independent ΔH is assumed and calculated from the slope which is equal $-\Delta H/2.303R$.

The choice of solubility unit is of some importance for it determines the reference standard state change; mole fraction, X_2, Henry's constant, K_1, molarity, C, and Ostwald coefficient, L, are commonly used. Plots of log X_2 and log K_1 against $1/T$ have slopes of equal magnitude but opposite sign. The same is true of log C_2 and log K_2 plots. Enthalpies from the concentration plots, X_2 or C_2, represent the standard state change of gas to solution; the K plots give enthalpies of the reverse reactions. Plots of log L against $1/T$ are commonly linear. To put the ΔH from such a plot on a mole fraction basis one must add RT.

$$X_2 = \frac{LP_{\mathrm{g}}V^{\mathrm{l}}}{RT} \text{ and } \frac{\mathrm{d} \ln X_2}{\mathrm{d}T} = \frac{\mathrm{d} \ln L}{\mathrm{d}T} - \frac{1}{T} = \frac{\Delta H}{RT^2}$$

Where exceptionally accurate solubility data from over an extended temperature range are available, an equation of the type

$$\log X_2 = \frac{a}{T} + b \log T - c \qquad \text{(Eq 24)}$$

can be fitted to the data where a, b, and c are the constants. Standard thermodynamic manipulations of this equation give the temperature-dependent heat of solution as

$$\Delta H = -2.303Ra + bRT$$

and the heat capacity change on solution as

$$\Delta C_{\mathrm{p}} = bR$$

The accuracy of the data is seldom good enough to attach any more than qualitative significance to the ΔC_p value.

Sherwood and Prausnitz (566) have carefully analyzed the factors important in getting the enthalpy of solution from phase-equilibrium data at high pressure. Their general expression for the partial molal heat of solution is

$$\frac{\Delta \bar{H}_2}{R} = \left[1 + \left(\frac{\partial \ln \phi_2}{\partial \ln Y_2}\right)_{T,P}\right]\left(\frac{\partial \ln Y_2}{\partial\, 1/T}\right)_P - \left[1 + \left(\frac{\partial \ln \gamma_2}{\partial \ln X_2}\right)_{T,P}\right]\left(\frac{\partial \ln X_2}{\partial\, 1/T}\right)_P \quad \text{(Eq 25)}$$

where ϕ_2 is the vapor phase activity coefficient, γ the liquid phase activity coefficient, and Y the vapor phase mole fraction. They used the equation to calculate the heat of solution of methane in decane at 1000 psia by approximating the vapor phase equation of state of moderate vapor densities by a virial expression through the second virial coefficient. Liquid phase corrections for $(\partial \ln \gamma_2/\partial \ln X_2)_{T,P}$ were obtained which required knowledge of the solution compressibility, partial molal volume of the gas in solution, and phase-equilbrium data. The calculated $\Delta \bar{H}_2$ had an uncertainty of 10% which mostly reflected the 1% uncertainty in the experimental liquid phase compositions. At higher vapor densities the third virial coefficient becomes important. The approach, which includes the effect of vapor and liquid nonideality, permits a relatively accurate calculation of the heats of solution for systems for which the experimental data are sufficiently accurate to warrant its use.

Namiot (438) gives a thermodynamic interpretation of the observed minimum in the solubility of hydrocarbons in water at about 70°.

The effect of temperature on salt effects and on the solubility of gases in molten salts is discussed in the appropriate sections.

C. PARTIAL MOLAL VOLUMES OF GASES DISSOLVED IN LIQUIDS

An understanding of the partial molal volume of gases in solution is of importance in the study of solution thermodynamic properties. Smith and Walkley (577) have tested the predictions of various thermodynamic theories of solution for the gas partial molal volume. They used available partial molal volumes of gases in nonpolar liquids and showed that a simple free volume theory predicted the correct magnitude and order of partial molal volumes in the various nonpolar liquids. In general, regular solution theory did not predict acceptable values of both solubility and partial molal volumes of a gas from a single value of gas solubility parameter. Hillier and Walkley (244A) have used a quantum equation of state and found good agreement between their predicted and the experimental partial molal volumes for H_2 and D_2 in liquid argon.

Hildebrand and Scott (244) discuss the contribution of volume expansion on mixing to the entropy of solution. Although volume expansion has little effect on the free energy of mixing, it can have a marked effect on the entropy of mixing. The correction to the partial molal entropy of solution of a dilute solute needs values of solvent internal pressure, $(\partial P/\partial T)_v$, and solute partial molal volume, $\bar{V}_2$.

Table VIII catalogs references to gas–liquid systems for which partial molal volumes are reported. Included is the extensive 1931 work of Horiuti (261); references to other pre-1940 data can be found in Kritchevsky and Ilinskaya (336). Two techniques have been used at atmospheric pressure. Most workers have used some modification of Horiuti's apparatus (261) to directly determine solution dilation on dissolving the gas to near saturation. Some have determined solution density (396). Details of the technique and apparatus are discussed in references listed in Table VIII.

Gamburg (198A) and Connolly and Kandalic (101) describe apparatus for the determination of partial molal volumes at high pressure. Some of the partial molal volumes at high pressure listed in Table VIII were not determined directly but got by fitting the experimental gas solubility to some form of the Krichevsky and Kasarnovskey quation (335, 336) for gas solubility at at high pressure.

D. GAS SOLUBILITIES IN MIXED NONELECTROLYTE SOLVENTS

A solution of a gas in a binary nonelectrolyte mixed solvent is a three-component system, with two gas–solvent interactions and a solvent–solvent interaction of importance.

Ben-Naim and Baer (39) have determined the solubility of argon in water–ethanol mixtures at six temperatures and nine concentrations between 0.015 and 0.25 mole fraction ethanol (Figure 11). At low temperatures there is a maximum in the solubility at low ethanol concentrations. Both viscosity and water partial molal volumes show a similar concentration dependence in the ethanol–water system. These results are explainable in terms of the influence of ethanol on the structure of water. Small amounts of ethanol increase the concentration of the icelike form of water at low temperatures; at about 30° the icelike structure of water is breaking down anyway and the argon solubility tends to increase monotonically from its value in pure warer to its value in pure ethanol. Dissolved argon itself influences the amount of icelike water present. Plots of $\Delta \bar{S}°$ and $\Delta \bar{H}°$ for the argon solutions show similar trends when plotted against the mole fraction of ethanol. The entropies of solution of argon in pure water are negative as compared to pure

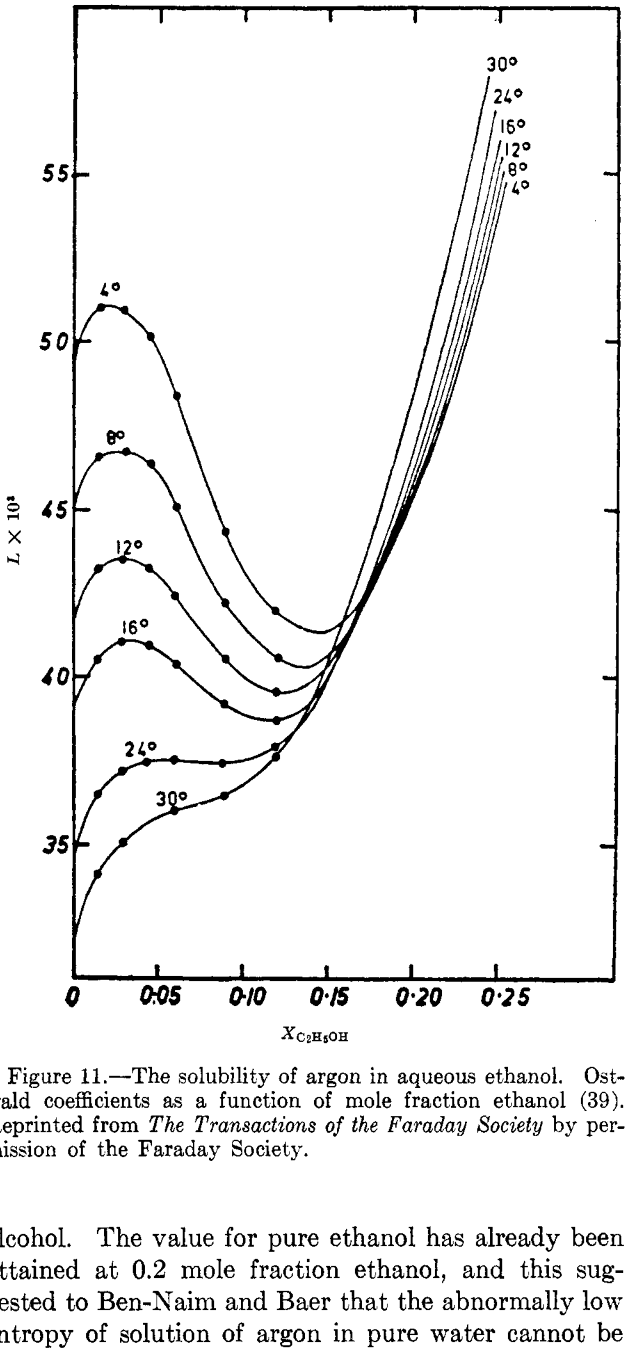

Figure 11.—The solubility of argon in aqueous ethanol. Ostwald coefficients as a function of mole fraction ethanol (39). Reprinted from *The Transactions of the Faraday Society* by permission of the Faraday Society.

alcohol. The value for pure ethanol has already been attained at 0.2 mole fraction ethanol, and this suggested to Ben-Naim and Baer that the abnormally low entropy of solution of argon in pure water cannot be attributed to an active formation of icelike water but that the argon shifts the already existing equilibrium toward the icelike form. A similar study of argon solubility in water–*p*-dioxane system is reported by Ben-Naim and Moran (40). The maximum in the argon solubility at low concentrations and low temperatures seen in the water–ethanol system was not found in the water–dioxane system. This is interpreted to mean *p*-dioxane has a destabilizing influence on the large compact clusters of water molecules at all *p*-dioxane concentrations and temperatures studied.

Schläpfer, Audykowski, and Bukowiecki (539) determined the solubility of oxygen from air at 30° over the full concentration range of aqueous solutions with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, ethylene glycol, and glycerine. The oxygen solubility decreases almost linearly with increasing weight per cent ethylene glycol or glycerine. In the monohydric alcohols the solubility behavior is somewhat similar to the argon solubility in ethanol–water at 32° with the solubility going through a minimum then increasing to the solubility in pure alcohol.

Some limited studies of gas solubility in aqueous alcohol mixtures include N_2 (168), N_2 and O_2 (342), and CO_2 (503) in ethanol–water, O_2 in methanol–water (478), and various gases in beers and wines (2, 168, 172, 313, 407).

Studies in other aqueous mixed solvents include: oxygen (248, 285) and CO_2 (379) in aqueous sugar solutions; He and Ar in water-saturated nitromethane (197); CO_2, acetylene, and ethylene in water–N-methylpyrrolidone (565); CO_2 in various aqueous mono-, di-, and triethanolamine solutions (381, 568, 596); acetylene in aqueous dimethylformamide, dioxane, and acetone (387), acetylene, methylacetylene, vinylacetylene, and diacetylene in aqueous dimethylformamide and N-methyl-2-pyrrolidinone (72, 72A); hydrogen sulfide in aqueous phenol (226) and in aqueous monoethanolamine (283); ClO_2 in aqueous acetic acid (305); and O_2 in aqueous H_3PO_4 (235). Solubilities in aqueous strong acid solutions are discussed under salt effects.

For less polar mixed solvents O'Connell and Prausnitz (459) have considered the thermodynamics of a solution consisting of one supercritical component, a gas, and two or more subcritical components, the liquid solvent components. They treat the case of a gas dissolved in two miscible solvents and generalize the result to a gas dissolved in a mixture of any number of miscible solvents. In their notation subscript 1 is the solvent of lower vapor pressure, 2 is the gas, and 3 the solvent of higher vapor pressure. The solvent activity coefficients are both referred to the saturation vapor pressure of solvent 1. The activity coefficient of the gaseous solute is also related to the saturation pressure of solvent 1 with the gas reference fugacity related to the Henry's constant in solvent 1 in the absence of solvent 3. Thus, they use an unsymmetrical convention for normalization of the activity coefficients $\gamma_1 \rightarrow 1$ as $X_1 \rightarrow 1$, $\gamma_2 \rightarrow 1$ as $X_2 \rightarrow 0$ at $X_3 = 0$, and $\gamma_3 \rightarrow 1$ as $X_3 \rightarrow 1$.

O'Connell and Prausnitz use the approach of Wohl and write one-paramenter Margules expansions for the excess free energy which in the symmetric convention

$$\frac{g_{12}^{E}}{RT} = \alpha_{12}X_1X_2 \quad \frac{g_{13}^{E}}{RT} = \alpha_{13}X_1X_3 \quad \frac{g_{23}^{E}}{RT} = \alpha_{23}X_2X_3 \qquad \text{(Eq 26)}$$

Then the molar excess free energy of the ternary solution is assumed to be

$$\frac{g_{123}^{E}}{RT} = \alpha_{12}X_1X_2 + \alpha_{13}X_1X_3 + \alpha_{23}X_2X_3 \qquad \text{(Eq 27)}$$

They differentiate and transform from the symmetric to the nonsymmetric convention to obtain expressions for γ_i as a function of the α's and mole fractions. The parameters α_{12}, α_{23}, and α_{13} are evaluated from the solubility data for the gas in pure solvent 1, the solubility data for the gas in pure solvent 3, and the vapor-liquid equilibrium data for the binary solution of 1 and 3, respectively. Finally Henry's law constant for the mixed solvent is

$$\ln H_{2,\,\text{mixed solvent}}\,(P_1^{s}) = X_1 \ln H_{21}(P_1^{s}) + X_3 \ln H_{23}(P_1^{s}) - \alpha_{13}X_1X_3 \qquad \text{(Eq 28)}$$

The equation shows that even if the two solvents form an ideal mixture ($\alpha_{13} = 0$), Henry's constant for the solute in the mixed solvent is an exponential rather than a linear function of the solvent composition. O'Connell and Prausnitz have calculated Henry's constant for H_2 in toluene–heptane and for O_2 in isooctane–perfluoroheptane, but no direct experimental confirmation is available.

Koudelka (333, 334) has determined the solubility of CO_2 in the six possible binary systems formed from methanol, acetone, chloroform, and benzene. He finds deviations for the activity coefficient of the gas in the binary solvent from the linear relation of activity coefficients in the pure liquids

$$\log \gamma_{2,\text{mixture}} = X_1 \log \gamma_{2 \text{ in } 1} + X_3 \log \gamma_{2 \text{ in } 3} \qquad \text{(Eq 29)}$$

The deviations may be expressed in terms of an excess function which requires only one constant, a, in a term aX_1X_3 for simple nonpolar solutions added to Eq 29.

Clever (95) determined the solubility of argon and krypton in binary p-xylene–p-dihalobenzene systems at 30°. The results fit regular solution theory with mixed-solvent solubility parameters obtained from mixed-solvent surface tensions.

Kruyer and Nobel (347) report that hydrogen solubility is a linear function of composition in benzene–cyclohexane mixtures. Hydrogen solubilities are also reported (9) for the aliphatic olefin mixtures hexane–hexene, heptane–heptene, and octane–octene.

Other studies in mixed solvents are CO_2 and N_2 in 50:50 decanol–dodecanol (378), N_2 and O_2 in 50:50 acetone–ethanol and isooctane–ethanol (342), acetylene in dioxane–dimethylformamide (387) and in various binary systems of water, methanol, CH_3Cl, and $(CH_3OCH_2CH_2)_2O$ with the donor-type solvents dimethylformamide, dimethyl sulfoxide, and ethylene glycol (517).

E. SOLVENT SURFACE TENSION AND GAS SOLUBILITY

A particularly successful gas solubility correlation is the linear relationship between log L and solvent surface tension, σ, for a gas in a series of solvents. Schläpfer, *et al.* (539), show that such a plot for oxygen solubility in about 20 solvents including alcohols, hydrocarbons, ketones, esters, and halocarbons holds well except for the solvents ethylene glycol, glycerine, and water. Baldwin and Daniel (23) correlate N_2, O_2, and air solubilities with the surface tension of lubricating oils and fuels. The solubility of the five gases He, Ne, Ar, Kr, and Xe fit the linear log L against σ plot almost within experimental error for 13 hydrocarbon solvents (96, 97) and for various substituted benzene solvents (530). Figure 12 shows such a plot for argon in 25 solvents.

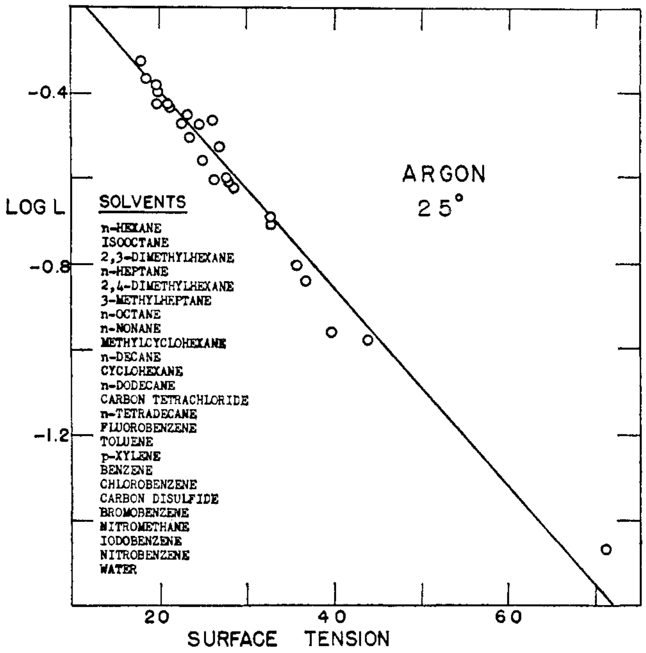

Figure 12.—Logarithm of argon Ostwald coefficients as a function of solvent surface tensions (530). Reprinted from *The Journal of Physical Chemistry* by permission of the copyright owners, The American Chemical Society.

Uhlig (620) assumed the energy of forming a solvent cavity for the gas molecule is equal to the cavity surface area times the liquid surface tension to derive

$$\log L = \frac{-4\pi r^2\sigma + E}{2.303kT} \qquad \text{(Eq 30)}$$

which predicts the linear log L against σ plots at constant temperature. The criticism that the bulk surface tension is not appropriate to calculate the energy of formation of a molecular-sized cavity seems justified. Rather the surface tension is probably proportional to some solvent property that determines the gas dissolving power of the solvent. Hildebrand and Scott (243, Chapter XXI) show that a plot of $\sigma/V_s^{1/3}$ against $\Delta E_{\text{vap}}/V$ for 19 liquids is linear with slope 0.86. This suggests the Hildebrand solubility parameter, δ, is proportional to $(\sigma/V_s^{1/3})^{0.43}$.

In mixed solvents the surface tension may not represent such a property of the bulk solvent because of Gibbs enrichment of the surface by the component of lower surface tension. Gjaldbaek (217) showed that decreasing water surface tension 57% by adding a trace of aeresol decreased carbon dioxide solubility by only 0.4% at 25° and 1 atm. Similar results were obtained for N_2 solubility in water (169). Although a trace of surface-active material does not change the equilibrium solubility of a gas in water, it may affect the rate of attaining equilibrium. The report of Yeh and Peterson (667) that CO_2, Kr, and Xe solubilities in lipids do not obey the Uhlig plot may be due to the presence of variable amounts of surface-active componets in the lipids. The Uhlig relationship is approximately obeyed for the solubility of Ar and Kr in the binary *p*-xylene–*p*-dihalobenzene systems (95). In these binary systems the solvent molecules are of similar size, shape, and surface tension. The surface enrichment of one component is minimal so the solution surface tension still represents a bulk property.

Burrows and Preece (85) base a derivation on the ideas of Eley (161, 162), and Uhlig, and the empirical relationship between surface tension and temperature, $\sigma = K/T^n$ that predicts a linear relationship between $\log L\ (T/\sigma)^{1/(n+1)}$ and σ/T_r where $n = {}^1/_2$ or 1. The solubility of helium in petroleum and silicone oils and of H_2, He, N_2, and methane in terphenyls (234) obeys the relationship. Plots of $\log L$ against $1/T$ were not linear for these systems.

Plots of the solubility of O_2, N_2, and air in six kerosene jet fuels against $1/\sigma^{0.75}$ are linear (144). Justification of the plot is the postulation that gas solubility is proportional to the solvent compressibility (β) and the relationship $\sigma\beta^{1/3}$ equals a constant.

The relationship of solvent surface tension and gas solublity in molten salts and in molten metals is discussed in the appropriate sections.

F. SALT EFFECTS

The activity coefficients of nonelectrolytes solutes in aqueous salt solution were well reviewed by Long and McDevit in 1952 (373).

The activity coefficient is a function of the concentration of all solute species and at a given temperature $\log f_{\rm i}$ can be represented by a power series in $C_{\rm s}$, the electrolyte concentration, and $C_{\rm i}$ the nonelectrolyte solute gas concentration.

$$\log f_{\rm i} = \sum_{mn=0} k_{nm} C_{\rm s}{}^n C_{\rm i}{}^m \qquad \text{(Eq 31)}$$

It is usually assumed that for low $C_{\rm s}$ and $C_{\rm i}$ where there is no chemical interaction between solute species only the linear terms are important and

$$\log f_{\rm i} = k_{\rm s} C_{\rm s} + k_{\rm i} C_{\rm i} \qquad \text{(Eq 32)}$$

The last term can be ignored if $k_{\rm i}$, which results from the interaction of the nonelectrolyte with itself, is small, or if $C_{\rm i}$ is very small. In gas solubility studies $C_{\rm i}$ is often small enough to justify ignoring the $k_{\rm i}$ term. Most theories are concerned with the calculation of $k_{\rm s}$. Experimental measurements of the solubility of a gas in pure solvent and in a salt solution give the activity coefficient of the dissolved gas directly. The gas solute activity is the same in pure solvent and salt solution so

$$f_{\rm i} S_{\rm i} = f_{\rm i}{}^\circ S_{\rm i}{}^\circ$$

and (Eq 33)

$$f_{\rm i} = f_{\rm i}{}^\circ \frac{S_{\rm i}{}^\circ}{S_{\rm i}}$$

where $S_{\rm i}{}^\circ$ and $S_{\rm i}$ are gas solubility in pure solvent and salt solution, respectively. Thus

$$\log f_{\rm i} = \log f_{\rm i}{}^\circ + \log \frac{S_{\rm i}{}^\circ}{S_{\rm i}} = k_{\rm s} C_{\rm s} + k_{\rm i} S_{\rm i} \qquad \text{(Eq 34)}$$

Since $\log f_{\rm i}{}^\circ = k_{\rm i}{}^\circ S_{\rm i}{}^\circ$

$$\log \frac{f_{\rm i}}{f_{\rm i}{}^\circ} = \log \frac{S_{\rm i}{}^\circ}{S_{\rm i}} = k_{\rm s} C_{\rm s} + k_{\rm i}(S_{\rm i} - S_{\rm i}{}^\circ) \qquad \text{(Eq 35)}$$

and if $S_{\rm i}$ and $S_{\rm i}{}^\circ$ are low the last term can be ignored

$$\log \frac{f_{\rm i}}{f_{\rm s}{}^\circ} = \log \frac{S_{\rm i}{}^\circ}{S_{\rm i}} = k_{\rm s} C_{\rm s} \qquad \text{(Eq 36)}$$

which is the same form as the well-know empirical Setschenow equation, $\log S_{\rm i}{}^\circ/S_{\rm i} = KC_{\rm s}$. However, in systems where the $k_{\rm i}(S_{\rm i} - S_{\rm i}{}^\circ)$ term cannot be ignored K and $k_{\rm s}$ are not the same. The distinction becomes important when comparing salting out of a nonelectrolyte of low solubility with one of high solubility. A salt that increases the activity coefficient of the dissolved gas salts out and a salt that decreases the activity coefficient of the dissolved gas salts in.

Long and McDevit (373) point out that the theories of the salt effect all have common underlying aspects but emphasize different approaches to the problem. They classify the theoretical approaches as emphasizing (1) hydration, (2) electrostatic, (3) van der Waals, and (4) internal pressure effects.

The hydration theories propose that salting out results from the effective removal of water molecules from their solvent role owing to the hydration of the ions. The theories provide no explanation of salting in.

The electrostatic theories relate salt effects to the influence of nonelectrolyte on the dielectric constant of the solvent. A nonelectrolyte that increases the dielectric constant of the solvent will be salted in, one that decreases the dielectric constant will be salted out.

The van der Waals theories extend the electrostatic theories by taking into account short-range forces, primarily dispersion forces, that may play an appreciable role in the specific effects of ions. The most detailed attempt to include dispersion forces is that of Bockris, Bowler-Reed, and Kitchener (53).

The interal pressure of a salt solution can be related to changes in both volume and compressibility of a solvent due to dissolved salts. Both changes have been correlated with salt effects. McDevit and Long (408) have calculated the free energy of transfer of a nonpolar electrolyte from pure water to salt solution assuming the neutral molecules modify the ion–water interaction in a simple manner and get a limiting law for k_s which is

$$k_s = \frac{\bar{V}_i^\circ(V_s - \bar{V}_s^\circ)}{2.3\beta_0 RT} \qquad \text{(Eq 37)}$$

where $\bar{V}_i^\circ$ and $\bar{V}_s^\circ$ are, respectively, partial molal volumes at infinite dilution of nonelectrolyte solute and salt, V_s is the molar volume of pure (liquid) electrolyte, and β_0 is the compressibility of pure water. Both the van der Waals and internal pressure approaches explain both salting-in and salting-out effects.

No new basic theories of salt effects have appeared since 1952, but several experimental tests based on gas solubility have been carried out.

Morrison and co-workers (426, 428, 430) have studied the salting out of H_2, He, Ne, N_2, O_2, Kr, Xe, SF_6, CH_4, C_2H_4, C_2H_6, C_3H_8, n-C_4H_{10}, and benzene vapor in some or all of the aqueous solutions of HCl, NH_4Cl, several alkali halides, $BaCl_2$, $LaCl_3$, and several tetralkylammonium chlorides. Electrostatic effects were tested by assuming k_s proportional to a coulombic term, $\Sigma ce^2/r$. Using crystallographic radii and using NaCl as a reference salt it was found that HCl, LiCl, $BaCl_2$, and $LaCl_3$ cause a salting out less than expected from ionic size. KCl behaves normally. KI is normal for low molecular weight gases, but causes a specific decrease in salting out which is proportional to the molecular size for the hydrocarbons and heavier organic gases.

Morrison and Johnstone (430) have calculated theoretical ratios of k_x/k_{NaCl} from electrostatic and internal pressure theories, where k_x represents the salting-out constant of HCl, LiCl, KCl, NH_4Cl, $^1/_2BaCl_2$, NMe_4Cl, NEt_4Cl, NaBr, NaI, $NaNO_3$, or $^1/_2Na_2SO_4$. The internal pressure results accord better with the observed order of ratios than the electrostatic approach but does not fit the NMe_4Cl and NEt_4Cl salt ratios for the more "inert" gases.

The k_x/k_{NaCl} ratio is linear for a series of solute gases in a given salt solution except the salts NaI, NMe_4Cl, and NEt_4Cl. With these salts a specific effect is observed. When a correction for the van der Waals forces between ions and neutral molecules is applied the k_x/k_{NaCl} ratios become linear for these salts.

The salt effect constant, k_s, can be referred to either unit volume of electrolyte solution or the unit weight of solvent. Morrison points out that the weight basis is more closely related to the theoretically significant mole fraction and reports his results on a solvent weight (molality) basis. On this basis nitric acid and tetraalkylammonium halides salt in He, Ne, n-C_4H_{10}, and benzene vapor but salt out SF_6.

The salting out of O_2, Ar, Xe, CH_4, and C_2H_6 by LiCl, NaCl, KCl, and $MgCl_2$ (173), C_2H_6 by NaCl and $CaCl_2$ (123), and C_2H_2 by numerous halide, nitrate, and sulfate salts (188) has been explained by hydration theories. Eucken and Hertzberg (173) have derived an expression for the hydration number of an ion based on an equilibrium association of water molecule clusters of one to eight molecules, the displacement of the equilibrium by the ions, and the competition of the ions and dissolved gas molecules for water of hydration. They get ion hydration numbers around 10. Flid and Golynets (188) point out that salting out increases in the order the cations increase in ease of hydration between 0 and 25°, but that the order differs in the 50–70° range. In general, as pointed out by McDevit and Long, the hydration numbers got ten by gas solubility measurements do not correspond with degrees of hydration obtained from other experiments.

Namiot (439) discusses aqueous gas solubilities in terms of a two-structure model of water. The dissolved gas molecules transform some "liquid" water molecules to "icelike" molecules. An equation is given for calculating the number of water molecules bonded to one gas molecule and the number of displaced water molecules. The Setschenow constant, K, is related to the number of bonded water molecules.

Clever and Reddy (99) have obtained salting-out constants for helium and argon by NaI in both methanol and water. The ratio k_{sMeOH}/k_{sH_2O} is less than expected from the dielectric constant difference of the solvents. The van der Waals approach of Bockris, Bowler-Reed, and Kitchener (53) was not sufficiently sensitive to explain the k_{sMeOH}/k_{sH_2O} ratio for either gas.

Many studies have been made on the effect of aqueous electrolyte solutions on the activity coefficients of dissolved hydrocarbon gases. With one exception the studies of Table III were carried out in aqueous solution.

Salting out is the general rule. Exceptions include Na dodecyl sulfate and K oleate, where micelle formation and increased interaction energy between the hydrocarbon gas and the hydrocarbon-like micelle interior may explain the enhanced solubility over that in pure water. Guanidine hydrochloride, nitric acid, and tetralkylammonium halides salt in hydrocarbons. The increased solubility of ethylene in silver nitrate solutions is certainly due to formation of the $Ag^+ \cdot C_2H_4$ complex ion. It is suggested (387) that the increased solubility of acetylene in acetone in the presence of NaI is because acetylene is more soluble in an acetone·NaI

TABLE III

SALT EFFECTS ON HYDROCARBON GASES

Gases	Salts	Ref
CH_4	NaCl, $CaCl_2$, $MgCl_2$	422
CH_4	NaCl	153
CH_4, C_2H_4	NaCl, LiCl, KI	428
CH_4, C_2H_6	Alkali halides	173
CH_4, C_2H_6, C_3H_8, C_4H_{10}	Guanidine hydrochloride	640
C_2H_6	NaCl, $CaCl_2$	123
C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}	Na dodecyl sulfate	660
C_3H_8, C_4H_{10}	NaCl	621
Cyclopropane	"Neutral salts"	268
Cyclopropane	NaCl	364
C_2H_4	KCl, $AgNO_3$	260
Propylene	"Neutral salts"	403
Propylene, C_4H_{10}, C_4H_8	K oleate	402
C_4H_8	NaCl	303
C_2H_2	"Neutral Salts"	188
C_2H_2	NaI (in acetone and dimethylformamide)	387
Ethyl acetylene	NaCl, NaOH	571
Benzene vapor, C_4H_{10}	HNO_3, tetralkyl ammonium halides	430

complex than in pure acetone. NaI has little effect on acetylene solubility in dimethylformamide.

The Setschenow equation does not apply to isobutylene solubilities in aqueous NaCl at temperatures near 0° (303).

The interest in oceanography has resulted in studies of nitrogen, oxygen, and noble gas solubilities in sea water and saline solutions (41, 42, 153, 327, 611). These systems salt out. Green (231) has made a careful study of oxygen solubility and Douglas (152) has determined nitrogen and argon solubility as a function of chlorinity (halide as g of chlorine/kg of sea water) and temperature. Green shows the oxygen solubility obeys a Setschenow-like equation with chlorinity used in place of salt molality.

The solubility of a gas over the range of 0 to 100% aqueous strong acid has been studied. The solubility of CO_2 initially decreases (salts out), goes through a minimum, increases to a maximum at a composition corresponding to $H_2SO_4 \cdot 4H_2O$, goes through a second minimum at a composition of $H_2SO_4 \cdot H_2O$, then increases until pure H_2SO_4 is reached (392, 555, 556). The minimums become less pronounced as the temperature increases (555). Na_2SO_4 in aqueous H_2SO_4 solutions of various composition salts out (556). CO_2 is salted in as the concentration of $HClO_4$ increases from 0 to 50 wt. %; it is salted out from 50 to 70 wt. % (392). The solubility of chlorine in aqueous 0 to 50 wt. %; $HClO_4$ decreases sharply up to 5 *M* and then stays constant to higher $HClO_4$ concentrations (551). Oxygen solubility decreases to a minimum at about 80% H_2SO_4 and then increases sharply as 100% H_2SO_4 is approached. Oxygen solubility decreases steadily as H_3PO_4 concentration increases (235).

Solubilities of oxygen in various nitric acid (502) and in white and red fuming nitric acid (579) are reported. ClO_2 solubilities in aqueous H_2SO_4 and aqueous acetic acid obey Henry's law (305).

The neutral nature of PH_3 has been deduced from its similar solubility in aqueous NaOH, NaCl, and H_2SO_4 (639). The solubility of N_2 in buffered solutions of various transition metal acetates indicated no unusual association of N_2 and transition ion (70).

Chlorine is salted out by $BaCl_2$ (51), LiCl, $SrCl_2$ and $BaCl_2$ (292), and $LiClO_4$ and $NaClO_4$ (291) in aqueous solution between 10 and 50°.

The temperature dependence of the salting-out constant, k_s, is small and negative at least in aqueous solutions at atmospheric pressure and temperatures below 70°. This is true of N_2O and CO_2 in several chlorides, nitrates, and sulfates between 0 and 40° (391), Cl_2 between 10 and 50° (51, 291, 292), and CO_2 in sulfuric acid between 20 and 60° (555). The salting out of acetylene is more pronounced between 0 and 25° than at higher temperatures up to 70° for 23 salts. The acetylene solubility goes through a minimum between 25 and 70° with the minimum becoming weaker at higher concentrations of the salt; no minimum is observed for NaCl, $ZnCl_2$, $ZnSO_4$, $MgSO_4$, $NiSO_4$, $CaSO_4$, and $Al_2(SO_4)_3$ (188). Sulfur dioxide is salted out at low temperatures but salts in with $NaHSO_3$ at 90° (348).

Long and McDevit (373) differentiate with respect to temperature their internal pressure expression for k_s, Eq 37, to get

$$\frac{dk_s}{dT} \cong -\frac{\bar{V}_i^\circ}{2.3RT}\left(\frac{d\bar{V}_s^\circ}{dT}\right) \qquad \text{(Eq 38)}$$

where $\bar{V}_i^\circ$ and $\bar{V}_s^\circ$ are, respectively, the partial molar volumes of nonelectrolyte and of electrolyte at infinite dilution. The relation predicts dk_s/dT to be small and negative, to be smaller in the 25–50° range than the 0–25° range, and that dk_s/dT will be small for LiCl and relatively large for KNO_3 with salts such as NaCl, KCl, KBr, KI, NaOH, and $^1/_2Na_2SO_4$ being intermediate in value. The predictions agreed well with the salt effect data of Markham and Kobe (391) on N_2O and CO_2 when reasonable partial molal volumes of the gases were used.

Morrison (426) gets approximate values for the difference in the heat capacity of solution between water and salt solution from the temperature dependence of gas solubility in water and in salt solution. He shows that ions that are thought to have a structure-building effect in water, such as Li^+, decrease the heat capacity of solution much more than salts thought to have a "structure-breaking" effect on water, such as I^-, which suggests that modification of the solvent structure in the vicinity of the nonelectrolyte molecules cannot be neglected in theories of salting out.

Salt effect studies at elevated temperatures and pressures are technically difficult. There is a problem in

TABLE IV

VALUES of $K = (1/m) \log K_s°/K°$

	Temp, °C							
	50	75	100	150	200	250	300	350
0.5 *m* NaCl	0.096	0.084	0.076	0.070	0.090	0.128	0.172	0.376
1 *m* NaCl	0.095	0.088	0.078	0.076	0.089	0.128	0.176	0.318
2 *m* NaCl	0.091	0.084	0.080	0.073	0.084	0.111	0.151	0.244

determining the partial pressure of the gas; a common practice is to simply subtract the steam table value from total gauge pressure to get the gas partial pressure. No correction is made for the effect of salt or dissolved gas on the steam table pressure.

Pray and co-workers (583) have determined the solubility of H_2 and O_2 in water and in about 0.17, 0.42, and 1.02 *M* solutions of both uranyl sulfate and uranyl fluoride between 100 and 280° and at pressures up to 3000 psi. He and Xe solubilities were determined in uranyl sulfate solutions up to 500 psi. With the exception of O_2 in uranyl fluoride solution, for which salting out is almost independent of temperature, salting out appears to increase with increasing temperature. Henry's law is applicable over only part of the pressure range; it fails at lower pressures as the uranyl salt concentration and temperature increase.

Anderson, Keeler, and Klach (14) have determined Kr and O_2 solubilities in aqueous uranyl sulfate solutions between 100 and 300°. Krypton obeyed Henry's law over the 10^{-4} to 10^{-1} psi partial pressure studied. Kr solubility was the same for water and in a solution which is 0.02 *M* in uranyl sulfate, 0.005 *M* in $CuSO_4$, and 0.005 *M* in H_2SO_4; when these concentrations were doubled Kr solubility increased. Oxygen solubility over the partial pressure range of 50–1500 psi was independent of the solvent.

Studies of CO_2 solubility in $CaCl_2$ solution to 700 atm (487) and air solubility in brine to 3500 psig (157) are reported.

Ellis and Golding (164, 165) have carefully studied the solubility of CO_2 in 0.5, 1.0, and 2.0 *M* NaCl up to 330°. They determined the density of NaCl solutions for temperatures to 350° and salt concentrations to 3 *M* to be able to interpret gas solubilities as volume distributions (Ostwald). They corrected water vapor pressures for dissolved CO_2 and NaCl assuming Raoult's law. They estimate maximum solubility errors may be as high as 5–10% in the 2 *M* NaCl at 300° because of uncertainties in the water vapor pressure. Their plot of Henry's law constant against temperature is Figure 13. The Setschenow salting-out *K* is calculated as $(1/m) \log K_s°/K°$ and results are in Table IV.

Salting out decreases with rising temperature but passes through a minimum of about 150° and then increases as the critical temperature of the solution is raised by the dissolved salt. The temperature of the minimum is similar to that for the minimum solubility of CO_2 in water.

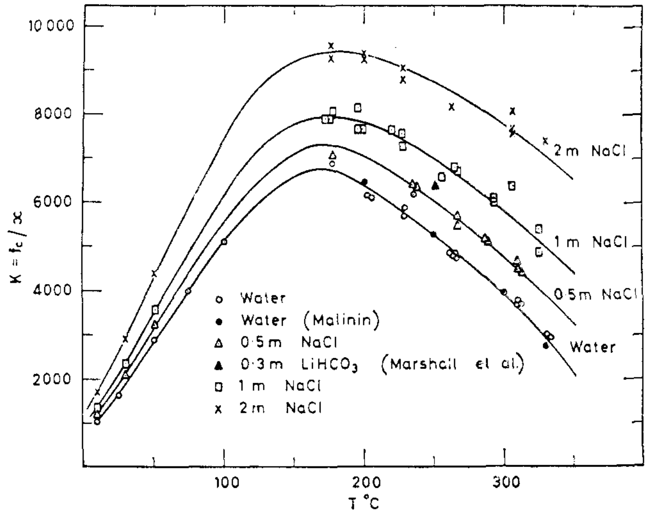

Figure 13.—Values of the Henry's law constant for the solution of carbon dioxide in water and in sodium chloride solutions between 10 and 335° (165). Reprinted from *The American Journal of Science* by permission of the editor.

Smith, Nagy, and co-workers (153, 578) have studied the effect of gas pressure on gas–aqueous salt systems near room temperature. They have determined the solubility of methane in aqueous NaCl, $CaCl_2$, and mixtures of $CaCl_2$ + NaCl and the solubility of nitrogen in NaCl, $CaCl_2$, Na_2SO_4, and $MgSO_4$ solutions as a function of pressure up to 1000 psia. Salting out occurs at all pressures, but there are negative departures from Henry's law for any given salt concentration as the N_2 pressure increases. Methane obeys Henry's law up to 200 psia. They estimate from their data that 1 ft^3 of sedimentary rock of 20% porosity, saturated with 50,000 ppm NaCl brine with the gas at the pressure at 1000-ft depth, can accommodate either 0.15 mole of N_2 or 0.30 mole of methane.

G. SOLUBILITY OF GASES IN BIOLOGICAL FLUIDS

The solubility of gases in biological fluids has been studied as an aid in understanding respiration in plants and animals, the anesthetic properties of various gases, the action of poisonous gases, and the unusual "salting-in" properties of detergent, denaturing, and protein solutions.

The solubility in various vegetable and animal fats and oils of the gases H_2 (619), Ra (452), N_2 and Ne (266, 267), cyclopropane (52, 364), H_2, O_2, and N_2

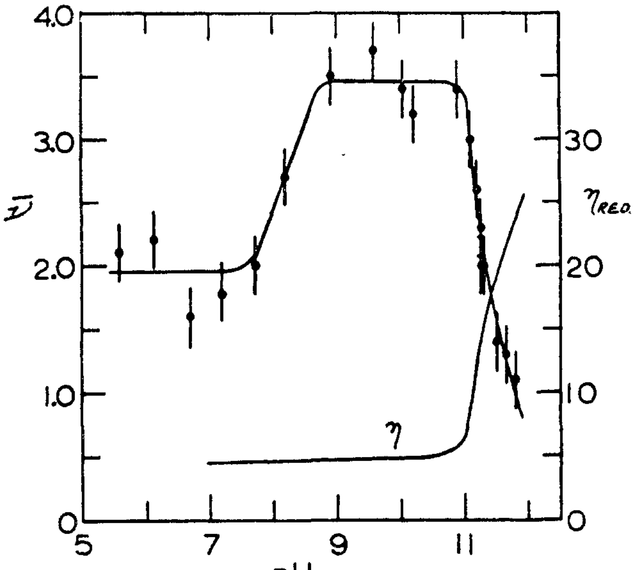

Figure 14.—Butane binding by bovine serum albumin as a function of pH. The ordinate is the average number of butane molecules bound per bovine serum albumin molecule, obtained from the excess solubility of butane in the protein solutions compared with the solubility in the protein-free solvent (641). Reprinted from *The Journal of Biological Chemistry* by permission of the copyright owners, The American Society of Biological Chemists, Inc.

(127), Xe (360), $CHCl_3$ and CH_3NO_2 (383), H_2, O_2, N_2, and CO_2 (532) have been measured. The solubility of the gases NH_3 (275), CS_2 (409), acetylene (486), cyclopropane (179, 268, 479), N_2O (17, 122, 567), CO_2 (18, 567, 570), Xe–O_2 mixtures (178), and N_2 (176, 567) has been reported for blood, various serums, and homogenized tissues. Leonard (363) analyzed the interstitial gases in fruits and, assuming these gases to be in equilibrium with dissolved gases, estimated the CO_2 and O_2 solubility in the fruit tissues. Gas solubility studies in biological systems are frequently small parts of larger studies and as a consequence overlooked in abstracting and indexing. Thus the listings above and in Table V may not be as complete as for some other fields.

The recent valuable studies of the solubility of simple hydrocarbons in protein, detergent, and denaturating solutions by Wishnia (659, 661) and Wetlaufer, *et al.* (640, 641), deserve special mention for the insight they give to hydrophobic bonding. Some aqueous solutions of proteins and detergents show an increase in the solubility of a gas over its solubility in water alone. Findlay noted such increases in CO_2 solubility in gelatin, hemoglobin, and methyl orange solutions before 1914 (see Markham and Kobe (393)). McBain (402–404) reported propylene solubilities in various detergents, and suggested that the enhanced solubility was due to the hydrocarbon gas entering inside of the hydrocarbon-like detergent micelle. Butadiene (507) is also "salted-in" by a detergent. The increased solubility of hydrocarbons in biological fluids was suggested to be due primarily to the high solubility of the gas in lipids (fats), but considerable evidence has accumulated to suggest that proteins have a special affinity for hydrocarbon and other gases (179, 268, 364, 567, 667).

Wishnia (659) determined the solubility of ethane, propane, and butane in water and in aqueous solutions of bovine serum albumin, human hemoglobin, lysozyme, and sodium lauryl sulfate at several temperatures between 10 and 35°. The increased solubility due to the protein in the solution was almost independent of temperature, and demonstrated that the transfer of dissolved gas from water to protein has a small enthalpy change and a large positive entropy change. Imai (268) has observed small enthalpies of transfer for cyclopropane in similar systems.

Wetlaufer, *et al.* (640, 641), studied the solubility of the hydrocarbon gases ethane, propane, butane, isobutane, pentane, isopentane, and neopentane in aqueous bovine serum albumin (BSA) and the denaturating solutions 7 *N* urea and 5 *N* guanidinum chloride. They point out that these eight gases represent six of the common amino acid side chains. The binding of butane by BSA is a function of pH (Figure 14) and falls off rapidly in pH regions where the protein goes to a random-coiled structure. Wetlaufer and Lovrien (641) suggest four possible mechanisms for the protein hydrocarbon interaction: (a) a dissolved nonpolar molecule could attach itself to one accessible surface of a nonpolar cluster, perhaps with partial penetration; (b) one nonpolar molecule might penetrate into one relatively nonpolar interior of the protein and lodge there; (c) a nonpolar molecule could be bound to a protein in the immediate neighborhood of an ion pair so as to strengthen this ion-pair interaction; and (d) hydrogen bonds and other polar interactions may be facilitated by placing a nonpolar group close to the interacting groups.

Wishnia's (660) study of ethane, propane, butane, and pentane in water and in aqueous sodium dodecyl sulfate as a model protein system appears to fit best with mechanism a or b, with (possibly) b being favored. Using the solubility and the temperature dependence of the hydrocarbon gas solubility in water, in aqueous detergent, and in hydrocarbons to obtain the free energy, enthalpy, and entropy changes in solution, he shows that the transfer of dissolved gas from water to detergent solution and from water to hydrocarbon are similar in thermodynamic behavior. The transfers have small, usually positive, enthalpy changes and a large positive entropy change. This suggests partial penetration, if not complete solution, of the low molecular weight hydrocarbon in the detergent micelle. Wetlaufer and Lovrien (64) calculate similar values of enthalpy and entropy change in the transfer of dissolved hydrocarbon gases from water to denaturing solutions of urea and guanidinium chloride.

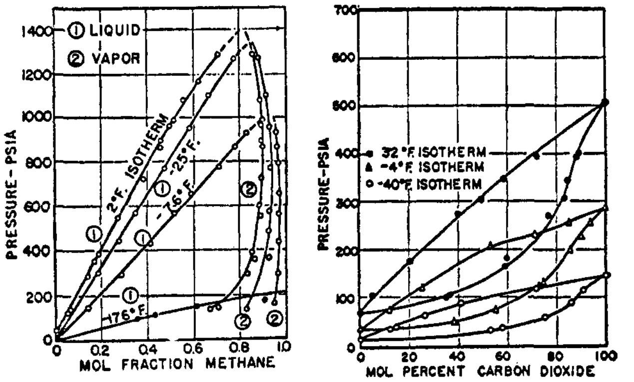

Figure 15.—Low-temperature phase equilibria. Pressure–composition diagrams for methane–propane system (left) and carbon dioxide–propane system (right) (5). Reprinted from *Industrial and Engineering Chemistry* by permission of the copyright owners, The American Chemical Society.

Featherstone, De Bon, *et al.* (179, 434), determined the solubility of the anesthetic gases N_2O, Xe, and cyclopropane in aqueous bovine serum albumin, hemoglobin, and γ-globulin. Only the hydrocarbon solubility increases as the albumin and hemoglobin concentration increases. Although the Xe solubility is not increased by the presence of hemoglobin, dielectric studies of the aqueous hemoglobin solutions (547) show that the nonrotating bound water is increased 17% by the presence of dissolved Xe. This evidence supports Pauling's hypothesis (471) that protein side chains, water, and inert gas interact to cause the formation of microcrystalline hydrates *in vivo*, and that these hydrates interfere with the normal electrical oscillations of the nervous system and thus lead to anesthesia.

H. EFFECTS OF PRESSURE ON GAS SOLUBILITY

Since 1940 so much good gas solubility work at high pressure has appeared and the understanding of gas solubility of both low and high pressures has so improved that references to both low- and high-pressure solubilities are included. However, the special techniques and apparatus needed for high-pressure solubility measurements will not be discussed. Krichevskii (338A) in a book (Russian) and Lachowicz (351) in a review have discussed solubility of gases at high pressure.

In this review gas solublity is taken as a special case of a vapor–liquid phase equilibrium where the gas phase is principally one component and the liquid phase principally the second component. Two component vapor–liquid systems in which both components have an appreciable concentration in both phases are not classed as gas solubility. In general, systems classed as gas solubility have components with a greater difference in critical temperature than those not classed as gas solubility. Examples of the two cases are shown in Figure 15. The methane–propane system (component's critical temperatures differ by 179°) is 80 mole % or more methane in the gas phase and is classed as gas solubility, but the carbon dioxide–propane system (critical temperatures differ by 66°) is not classed as gas solubility. For systems where the information left some doubt the data were usually included as gas solubility.

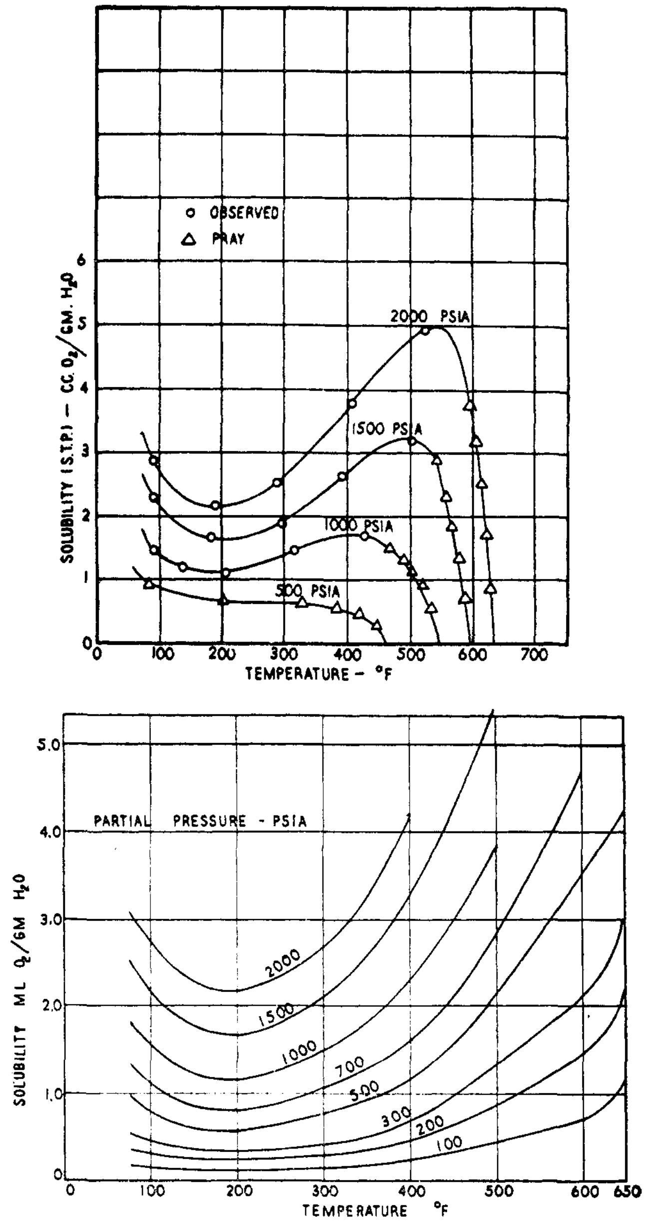

Figure 16.—Isobars of the water solubility of oxygen gas as a function of temperature. Total gauge pressure (upper) and "hypothetical" oxygen partial pressures (lower) (686). Reprinted from *The Transactions of the Society of Mechanical Engineers* by permission of the copyright owners, The American Society of Mechanical Engineers.

The reporting of high-pressure gas solubility presents difficulties when only the total pressure is directly measured. The effect of the high-pressure gas and dissolved gas on the true vapor pressure of the solvent is not known nor is it easily measured. Figure 16 shows isobars of oxygen solubility in water at total gauge pressure and at a fictitious oxygen partial pressure obtained by subtracting the saturation vapor pressure of water from the total pressure. The usual negative temperature coefficient of gas solubility in water is noted to about 100°, but at higher temperatures the solubility increases with temperature. Henry's law is apparently obeyed to only moderate pressures (686).

Krichevsky and Kasarnovsky (335) have developed a thermodynamic equation for calculating the solubility of slightly soluble gases at high pressure in solvents of low vapor pressure. Michels, Gerver, and Bijl (417) deduce a similar equation directly from the general equations for the equilibrium of a binary mixture. Sattler (526) gives a thermodynamic derivation for cases with both a negligible and a finite solvent vapor pressure. Needed for the calculation is low-pressure gas solubility data of the pure gas at low pressure and thermodynamic data of the pure gas at high pressure. Kobayashi and Katz (324) use the rigorous thermodynamic relation

$$[\mathrm{d}\bar{G}]_{T,X_2} = RT\mathrm{d}\ln \bar{f}_2 = \bar{V}_2\mathrm{d}P \qquad \text{(Eq 39)}$$

and Henry's law

$$f_2{}^\circ = KX_2 \qquad \text{(Eq 40)}$$

where $\bar{G}_2$ is the partial molal free energy of the dissolved gas, and P, T, and R are pressure, temperature, and gas constant, respectively. $\bar{V}_2$ and X_2 are partial molal volume and mole fraction of the dissolved gas, and $\bar{f}_2$ and $f_2{}^\circ$ are partial molal fugacities of the solute gas at the total pressure and at the solvent saturation pressure, respectively. Integration of Eq 39 between the limits of the solvent vapor pressure P° and the total pressure, P, assuming $\bar{V}_2$ to be independent of pressure and changes in solution concentration, followed by eliminating $f_2{}^\circ$ by Henry's law gives the Krichevsky–Kasarnovsky type equation

$$\ln\frac{\bar{f}_2}{X_2} = \ln K + \frac{\bar{V}_2(P - P^\circ)}{RT} \qquad \text{(Eq 41)}$$

The equation is sometimes used in the form below, where a modified Henry's constant K' is defined ln $K' - \bar{V}_2P^\circ/RT$.

$$\ln\frac{\bar{f}_2}{X_2} = \ln K' + \frac{\bar{V}_2P}{RT} \qquad \text{(Eq 42)}$$

The equation has been successfully used to fit high-pressure gas solubility in water, methanol, and hydrocarbons (324, 335, 339, 420, 441, 443). The modified Henry's constant, K', shows a family relationship for hydrogen dissolved in paraffin and in olefin solvents as a complicated function of temperature. It can be used to calculate hydrogen solubility in binary and ternary mixed hydrocarbon solvents with fair success (37).

Kritchevsky and Ilinskaya (336) point out the empirical nature of Eq 41. The partial molal volumes from the slope of a plot of ln f_2/x_2 against P seldom agree with the experimentally determined partial molal volumes. The difference is due to the concentration dependence of partial molal volumes and partial molal heats of solvent and solute in the dilute binary mixture. Departure of the $\bar{V}_2$ in Eq 41 and 42 from the experimental $\bar{V}_2$ is taken as a sensitive test for discovery of deviations from Henry's law. An equation for a slightly soluble gas in a liquid under pressure is derived that takes into account the concentration dependence of partial molal volume. It adds a term $-(A/RT)(1 - x_1{}^2)$ to the right-hand side of Eq 41. The equation is generalized to fit the solubility of mixtures of gases. Gonikberg (226A) showed that his modification of regular solution theory could be used to calculate the constant A. The Kritchevsky–Ilinskaya equation has been applied to ethylene solubilities in methanol, acetone, methyl ethyl ketone, and toluene (563, 564), to CO_2 solubilities in C_1 to C_4 hydrocarbons (606A), and to the H_2 solubility in cyclohexane (337) where the H_2 partial molal volume is strongly affected by pressure. Efremova (156) discusses the pressure dependence of partial molal volumes.

Orentlicher and Prausnitz (463) have extended the treatment of hydrogen solubilities in cryogenic liquids at high pressure by taking into account the effect of composition on the activity coefficients. For the small concentration range common to gas solubility they assume the activity coefficient of the solvent is given by the one-parameter expression

$$\ln \gamma_1 = \frac{A}{RT}X_2{}^2 \qquad \text{(Eq 43)}$$

and they use the modified Henry's law equation

$$\bar{f}_2 = \gamma_2{}^*Kx_2 \qquad \text{(Eq 44)}$$

This leads to an equation

$$\ln\frac{\bar{f}_2}{x_2} = \ln K + \frac{A}{RT}(X_1{}^2 - 1) + \frac{\bar{V}_2(P - P^\circ)}{RT} \qquad \text{(Eq 45)}$$

which is similar in form to the Kritchevsky–Ilinskaya equation. Orentlicher and Prausnitz show that for small solubilities the equation can be put in the form

$$\ln\frac{\bar{f}_2}{x_2} = \ln K + \left[\bar{V}_2 - \frac{2A}{(K/\phi_2{}^\circ)}\right]\left(\frac{P - P^\circ}{RT}\right) \qquad \text{(Eq 46)}$$

where $\phi_2{}^\circ$ is the vapor phase fugacity coefficient. Thus at small values of x_2 it predicts a linear ln $\bar{f}_2/x_2$ against P relationship.

Henry's law constant, K, the constant, A, and $\bar{V}_2$ are all temperature dependent. Orentlicher and Prausnitz estimate $\bar{V}_2$ assuming hydrogen to behave as a hard-sphere gas. They get K and A from the fit of the equation to the solubility of hydrogen in the solvents Ar, CO, N_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, and n-hexane. No significant variation of A with temperature was found. They developed a simplified solution theory that suggests a plot of a reduced Henry's constant, K_r (K divided by the solvent solubility parameter squared, evaluated at $0.7T_c$), against reduced temperature, T_r ($T_r = T/T_c$), should give a universal curve for all solvents. Their plot of K_r against T_r falls on at least two lines, one for the solvents ethane, ethylene, propane, and propylene and another for the inorganic liquids Ar, N_2, and CO. The difference in the lines is taken to indicate a qualitative difference between hydrogen–hydrocarbon and hydrogen–inorganic molecule intermolecular forces.

Himmelblau and Arends (250) have developed a five-constant equation to correlate the literature high-pressure solubility data of gases that do not react with water. Prausnitz, Edminster, and Chao (484) develop a solubility parameter expression for the vaporization equilibrium ratio that has application to high-pressure solubilities.

Some other equations that have been used to correlate high-pressure gas solubility include for CO_2 in methyl ethyl ketone, ethyl acetate, and toluene (559)

$$\ln f_2/x_2 = \ln K - \frac{A'x_2}{RT} \qquad \text{(Eq 47)}$$

for CO_2 in methanol (558)

$$x = 0.425(P/P°) \qquad \text{(Eq 48)}$$

Kiyama and Hiraoka (314) fit the solubility of acetylene in benzene with regular solution theory including Flory–Huggins mixing (Eq 21) when the compressibility factor, Z, is included in the solubility parameter calculation

$$\delta = \left[\frac{(\Delta H_{\text{vap}} - RT)Z}{V}\right]^{1/2} \qquad \text{(Eq 49)}$$

Lachowicz (351A) analyzed regular solution theory (Eq 20) and predicted deuterium should be more soluble than hydrogen. However, high-pressure solubility studies of H_2 and D_2 in heptane and octane showed no significant difference (352).

Namiot and Bondareva (440) compared simple hydrocarbon solubilities in water. At 200 atm and 40° the ratio of solubility for $CH_4/C_2H_6/C_3H_5/C_4H_{10}$ is 1:0.44:0.20:0.073. McKetta and co-workers have studied the solubility of methane (120, 121), ethane (119, 120), propane (20), ethylene (140), propylene (21), cyclopropane (269), 1-butene (74), 1,3-butadiene (493), and propyne (270) in water. The "normal" behavior of a solubility minimum at some temperatures is observed for methane, ethane, propane, propylene, ethylene, and 1-butene, but in the regions of temperature and pressure studied cyclopropane, propyne, and 1,3-butadiene show no minimum. Above the condensation pressure of the gas there is a three-phase system of gas–water-rich liquid–hydrocarbon-rich liquid. Figure 17 compares the pressure dependence of hydrocarbon solubility in water at 38°. Hydrocarbon solubility in water increases with unsaturation. 1,3-Butadiene is four times more soluble than n-butane, and acetylene is more soluble than the other hydrocarbon gases.

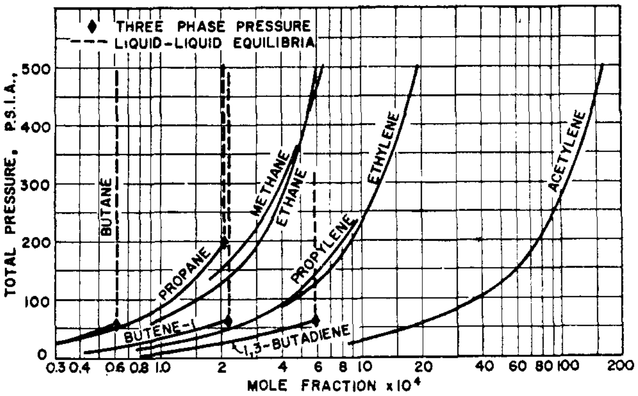

Figure 17.—Comparison of the solubility of various hydrocarbons in liquid water at 100°F (37.8°) as a function of pressure (493). Reprinted from the *Journal of Chemical Engineering and Data* by permission of the copyright owners, The American Chemical Society.

The solubility of ethylene up to 120 atm is in the order hexane > cyclohexane > benzene (683). Hydrogen containing freons are much more soluble in water than other freons (469). The solubility of acetylene in acetone goes through a pronounced minimum at 3° and 15 atm. At higher temperatures the minimum tends to disappear (259).

A test for the thermodynamic consistency of the solubility data for the hydrogen–helium system has been made (69A). The surface tension lowering due to dissoved N_2 and argon up to 120 atm in water, hexane, octane, and methanol has been examined (397A).

Hiraoka and Kiyama (251–253, 313–315) have studied the pressure dependence of acetylene and ethylene solubility. Acetylene shows positive deviations from Raoult's law in water, methanol, and benzene, negative deviations in tetrahydrofuran. Heats of solution are exothermic in water and methanol, endothermic in benzene. Ryutani (512–517) finds that acetylene solubilities at high pressure show negative deviations from Raoult's law in electron-donating solvents. The acetylene solubilities are proportional to the O atoms/mole in polyethylene glycols unless steric factors were present. The acetylene solubility was less than expected from the pure solvent solubilities in binary mixtures of donor-type molecules with either chloroform, water, or methanol.

Some studies of the solubility of gas mixtures include observations that the presence of CO_2 decreases the solubility of N_2 more than N_2 decreases CO_2 solubility (679). Methane decreases CO_2 but ethane increases CO_2 solubility (394A). The solubility of CO_2 from a N_2–H_2 mixture is proportional to its fugacity calculated from the Beattie-Bridgman equation (673).

The solubility of CH_4–N_2–CO_2 mixed gas in water can be calculated from the solubility of the single gas and the activity coefficient of the components of the gas phase (437).

The Krichevsky–Kasarnovsky equation holds approximately for Ar–CH_4 (443) and for He–CH_4 (441) mixed gas solutes. Trivus (607) has tested the Kritchevsky–Ilinskaya equation for mixed gases and finds it good to no better than 12% at low gas concentrations.

The effect of hydrostatic pressure on the solubility of a gas is of interest to oceanographers. Klots (317) has used a simple thermodynamic approach to calculate the change in Henry's law constant with depth.

$$\log \frac{K(P)}{K(0)} = \frac{P\bar{V}_2}{2.303RT} \qquad \text{(Eq 50)}$$

$K(P)$ and $K(0)$ are Henry's law constant at 0 and P hydrostatic pressure; $\bar{V}_2$ is the gas partial molal volume, assumed independent of pressure. His calculation shows that with surface water in equilbrium with gas at 1 atm, equilibrium solubility decreases (Henry's constant increases) with water depth for both nitrogen and oxygen.

Klotz (321) also assumed gas equilibrium exists between surface and ocean depths. He takes into account the dependence of Gibbs free energy on depth (the position of the solute in the gravitational field), on pressure, and on the amount of solute dissolved in a specified amount of solvent at a particular depth. His thermodynamic derivation gives

$$\ln \frac{m_{\text{depth}}}{m_{\text{surface}}} = \frac{M_2 g}{RT}(1 - \bar{V}_2\rho)d \qquad \text{(Eq 51)}$$

where m_{depth} and m_{surface} are molalities; M_2 is the gas molecular weight, g acceleration due to gravity, $\bar{V}_2$ the gas partial molal volume in cm^3/g, ρ the solvent density, and d the solvent depth in cm. Both $\bar{V}_2$ and ρ are assumed independent of pressure. The sign of the term $(1 - \bar{V}_2\rho)$ determines whether the gas will increase or decrease in solubility with depth. The equation predicts H_2, CO, and N_2 solubilities to decrease with depth, CO_2 solubility to increase with depth, and O_2 solubility to be almost independent of depth.

An experimental study of the effect of hydrostatic pressure on gases dissolved in water by Enns, Scholander, and Bradstreet (169) indicated He, N_2, O_2, Ar, and CO_2 all decrease in equilibrium solubility with depth. Actually, they determined the gas equilibrium pressure necessary to maintain the atmospheric gas pressure saturation value as the hydrostatic pressure increased from 0 to 1500 psig. The required equilibrium gas pressure increased 13% for He, 14% for N_2, O_2, and Ar, and 16% for CO_2. This would presumably imply the same percentage decrease in solubility in order to maintain a gas equilibrium pressure of 1 atm.

I. SOLUBILITY OF GASES IN MOLTEN SALTS AND GLASSES

The determinations of gas solubility in molten salts and glasses has been done primarily by workers interested in molten salt reactors, industrial processes using molten salt solvents as the aluminum industry, or glass technology.

The most extensive work on gas solubilities in molten salts was carried out by Grimes and co-workers at Oak Ridge. They have determined the solubility of helium, neon, argon, and xenon in molten fluoride salt mixtures LiF–NaF–KF (50), NaF–ZrF_4 (232), and LiF–BeF_2 (635). They have also determined solubilities of HF in NaF–ZrF_4 mixed melts (553) and BF_3 in a LiF–BeF_2–ZrF_4–ThF_4–UF_4 melt (554).

The noble gas solubilities are of the order of 10^{-8} to 10^{-7} mole of gas per cc of melt with the solubility decreasing in the order He > Ne > Ar > Xe. The enthalpies of solution for all four gases are positive and become more positive as the gas atomic weight increases. Solubility increases with temperature. Henry's law is obeyed over the 0.5–2-atm range studied.

Grimes and co-workers have picked a standard state change for calculation of the thermodynamic properties of the solution so that the entropy of solution is purely a function of solvent–gas interactions. The standard state change is

$$X_{(\mathrm{g},\mathrm{C_d})} \rightarrow X_{(\mathrm{d},\mathrm{C},\mathrm{d})}$$

where X represents 1 mole of gas. The subscripts g and d denote the gas and liquid phases and C_d is the concentration of the gas dissolved in the liquid which is in equilibrium with the gas at concentration C_g. They assume the change from C_g to C_d in the gas phase is ideal. Thus, in the desired standard state

$$\Delta\bar{S}° = \frac{\Delta\bar{H}°}{T} + R \ln C_\mathrm{d}/C_\mathrm{g} \qquad \text{(Eq 52)}$$

where $\Delta\bar{H}°$ is the heat of solution gotten from a plot of log Henry's law constant against $1/T$ (50). The entropies of solution at 1000°K in NaF–KF–LiF and NaF–ZrF_4 melts vary from -0.1 to -1.5 cal/deg/mole with no regular pattern for the four gases. In the LiF–BeF_2 melts the entropies are more negative, varying over the range -3.1 to -4.2 for the four gases.

Grimes and co-workers (50, 635), using a model similar to that of Uhlig (620), correlate the noble gas solubilities by equating the free energy of solution of the gas to the free energy of formation of holes which were assumed to be of the same size as the gas molecule in a continuous fluid having the same surface tension as the solvent. The approach gives an expression for the Henry's law constant as a function of the liquid surface tension, σ, the radius of a spherical gas atom, r, and the temperature, T.

$$K_c = \frac{C_d}{C_g} = \exp\left(-\frac{18.08r^2\sigma}{RT}\right) \qquad \text{(Eq 53)}$$

Although admittedly a naive model, it does remarkably well at correlating the noble gas solubility in molten salts. Taking the noble gas atomic radii as the same as in the solid and assuming the values to be the lower limit of the hole radius, the correct magnitude and order of solubility are predicted for the He, Ne, Ar, and Xe series. This is not the same order observed in nonelectrolyte solvents at room temperatures where the normal surface tension range is 15–40 ergs/cm². The molten salts studied have surface tensions between 112 and 180 ergs/cm² and the free energy of forming holes is presumably a predominant term. The calculated Henry's law constant for helium and neon is high. A larger radius for helium and neon can be justified on the basis of thermal motion of these less polarizable atoms in the melt, and this would give better agreement between the calculated and experimental constants.

The HF (553) and BF_3 (554), solubilities in molten fluorides obey Henry's law. The heats of solution are exothermic and the solubilities of both gases decrease with temperature. The entropies of solution at 1000°K are about -6 for HF and about -22 for BF_3, both values being more negative than values for the noble gases in similar mixed melts. BF_3 is much more soluble than the noble gases. The solubility of HF increases tenfold as the NaF concentration increases from 45 to 80.5 mole % in the NaF–ZrF_4 system. The increase is thought to be related to the high stability of HF–NaF compounds.

Woelk (662) reports argon solubilities and discusses the relation of molten salt free volume to gas solubility. Scholze and Mulfinger (545) report the solubility of helium decreases when the concentration of lithium in a mixed silicate melt increases from 20 to 25 mole % as Li_2O. However, the glass molar volume per two oxide ions shows negligible change from that of pure SiO_2. Assuming that lithium also enters cavities where the helium atom fits, the decrease in helium solubility was used to calculate the lithium ion radius, and a reasonable value of 0.76 A was obtained.

Scholze and Mulfinger (435, 546) describe an apparatus sensitive to 10^{-4} cc of helium and report the solubility of helium in various binary and ternary silicate melts between 1200 and 1480°. The helium solubility increases with temperature and there is a relation between the temperature dependence of helium solubility and the thermal coefficient of expansion of the glasses investigated. In lithium silicate melts the amount of dissolved helium depends on the volume of interstices in the atomic constitution of the melt. Conditions for a purely physical solubility are fulfilled.

The solubility of helium in Pyrex (506) is reported to be independent of temperature between 25 and 515°.

The solubility of hydrogen in molten alkali metal hydroxides is stated to be less than 60 mg of hydrogen/100 g of alkali hydroxide unless corrosion products are present. Corrosion products increase the solubility of hydrogen (589). In Pyrex glass at 1170° hydrogen at 10 mm pressure has a solubility of 0.060 ml (STP)/g, but there was no measureable solubility of helium, oxygen, or argon (444). An observed increase in hydrogen solubility in CaO–Al_2O_3–SiO_2 slags as the CaO content increased was explained on the basis that the Ca–O–H grouping was more stable than the Si–O–H grouping (451).

Ryabukhin (511) finds the solubility of chlorine in melts of NaCl, KCl, and $MgCl_2$ and their 1:1 mixtures show little salt dependence. Plots of log ST against $1/T$ are linear and the solubility, S, can be represented by

$$S = \left(\frac{1.19 \times 10^{-2}}{T}\right)e^{-A}$$

where $A = (Q + Q_1T)/RT$ and Q and Q_1 are work functions.

Oxygen and nitrogen have a solubility of less than 10^{-4} mole/mole of salt at the freezing point in sodium, potassium, and cesium nitrates (195). Oxygen has a "negligible" solubility in glass (444).

Mahieux (385) determined the solubility of carbon dioxide in molten glass by a $^{14}CO_2$ tracer technique. He found the solubility decreased with temperature over the 1100–1300° range. Krohn, Grjotheim, and co-workers (233, 364) observe that the solubility of carbon dioxide at 1 atm in molten NaCl and molten KCl increases with increasing temperature with the heat of solution being twice as great in KCl as in NaCl. The solubility is greater in NaCl at 800° but greater in KCl at 950°. They correlate the crossover in solubility with temperature to a similar crossover in free volume with temperature for the two salts.

The solubility of water vapor in molten salts and glasses has received considerable attention. Scholze and Mulfinger (546) determined the solubility of water vapor in various binary and ternary silicate melts between 1250 and 1750°. They found the water vapor solubility increases with increasing alkali content of the glass, with increasing radius of the alkali ions, and with increasing temperature. The solubility depends on the square root of the water vapor pressure and can be used as a measure of melt basicity.

Tomlinson (602) reports the solubility of water in sodium silicate decreases 10% on going from 900 to 1100°. The solubility is not proportional to the square root of water vapor pressure especially at the lower vapor pressures possibly because some sodium vapor is formed which reacts and removes water vapor in cool parts of the solubility apparatus.

Duke and Doan (154) find water vapor solubility is negligible in either $NaNO_3$ or KNO_3 until $LiNO_3$ is added. In the mixtures containing $LiNO_3$ the solubility is measurable and linear with temperature. The solubility varies with $[Li^+]^2$ which suggest two Li^+ ions are involved for each water molecule. It is pointed out that lithium has a greater ion–dipole interaction with water than the other alkali metal ions.

The solubility of water vapor at 20 mm in $NaNO_3$, KNO_3, and $CsNO_3$ at their freezing point is found to be near 10^{-3} mole/mole of salt by Frame, Rhodes, and Ubbelohde (195). The solubility is proportional to the free volume in the melt. When divalent cations are added, *e.g.*, Ba^{+2}, there is a slight increase in water solubility. There is probably only a slight increase in vacancies because of the considerable electrostriction of the melt that takes place when a divalent ion is added.

The solubility of water vapor in LiCl–KCl melts was determined between 3 and 26 mm at 390 and 480°. Henry' law is obeyed up to 10 mm at 390 and up to 18 mm at 480° according to Burkhard and Corbett (82, 83). At the higher pressures HCl is detected and it is thought that lithium hydrolyzes. The solubility of HCl has been determined in the same melts. Henry's law is obeyed up to 90 mm for HCl but the straight line does not go through the origin at zero pressure indicating a residue of hydroxide was initially present in the melts. The hydroxide residue was not thought to have affected the water solubility.

Sulfur trioxide in glass is in the form of a SO_2–O_2 mixture (45).

J. THE SOLUBILITY OF GASES IN MOLTEN METALS AND ALLOYS

Table VII lists references to the solubility of gases in molten metals and alloys. The solubility of a gas in a molten metal may represent a physical equilibrium between the gas and metal alone, or it may represent an equilibrium between metal and an intermediate oxide, nitride, or hydride phase for which at constant temperature there is a fixed pressure of the corresponding gas. Especially helpful introductions to the subject of gases in liquid metals are two papers from a 1954 Australian symposium on gases in metals by Willis (655) and by Jenkins (278A). These papers, which also discuss adsorption on metals and gases in solid metals, summarize the theoretical approaches and list references to earlier review papers. The books of Turovtseva and Kunin (618A) and of Smithells (578A) contain information on the solubility of gases in liquid metals.

The diatomic gases usually are in the liquid metal in the atomic state. Their solubility obeys Sievert's square root of pressure law

$$S = K\sqrt{p}$$

It can be shown (278A) that Sievert's experimental law is an expression for Henry's law when the solution equilibrium for the atomic solution of the gas is taken into account

$$H_2(g) \rightleftarrows 2H\ (soln)$$

A detailed discussion of H_2, N_2, and O_2 gas solubilities in liquid metals is beyond the scope of this review. For details see references listed in Table VII.

The solubility of the rare gases in liquid metals is quite low. No absorption of helium by mercury was detected at 25 atm and room temperature (431). McMillan (410A) calculated the solubility of xenon in liquid bismuth to be 3×10^{-16} atomic fraction at 300° and 1 atm pressure by a free volume model for liquid bismuth. Experimental solubility determinations give 3×10^{-8} atomic fraction at 540° and 1 atm (171), 4×10^{-9} (422A) and 2×10^{-10} (242A) atomic fraction at 500° and 1 atm pressure. The lowest value seems most reliable at this time. Surface adsorption and occlusion may be responsible for the higher results. McMillan also predicted high surface adsorption which has been confirmed (242A). Xenon solubilities in mercury and in sodium are also reported (422A).

Johnson and Shuttleworth (281) and Johnson (280) review briefly earlier work on rare gas solubility in liquid metals and report measurements of krypton solubility in liquid cadmium, indium, lead, tin, and silver by a technique using radioactive ^{85}Kr. Their lower limit of measurement was an Ostwald coefficient of 10^{-7} ($\sim 10^{-11}$ atomic fraction). No solubility was detected in silver, but Ostwald coefficients in the other metal melts varied from 10^{-7} to 10^{-5}. The temperature dependence of the Ostwald coefficient was used to get the energy, H, needed to transfer an atom at rest from the gas into the solution of the metal and the vibrational entropy, S, of the krypton atom dissolved in the liquid metal from

$$L = \frac{h^3}{(2\pi mKT)^{3/2}}\left(\frac{1}{a^3}\right) \exp(S/R) \exp\left(\frac{-H}{RT}\right)$$

where m is the mass of the krypton atom and $1/a^3$ is the number of metal atoms in unit volume of the liquid metal.

The experimental H was compared with a calculated H which considered the energy of transfer to be made up of three terms: (1) the energy to make a hole in the liquid the size of the krypton atom estimated from the hole area of krypton atom radius and the surface energy per unit area (surface tension) of the liquid metal extrapolated to 0°K; (2) the vibrational energy of a krypton atom in the liquid approximated as being the same as the vibrational energy of a metal atom as obtained from heat capacity data; and (3) the negative van der Waals interaction energy between the krypton atom and the surrounding metal atoms estimated from adsorption potentials of inert gases on metals. The estimated values of H agreed within a few kilocalories

TABLE V
SOLUBILITY DATA

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Inert Gases				
Helium	Water	1	5–73	2	429
		1	25	1	197
		7–34	163–316	1	481
	Water (hydrostatic pressure)	1–102	25	1	169
	D_2O	3.4–78	50–280	1	585
	Sea water	1	1–20	1	327
	Methanol	1	30	2	99
	n-Hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, *n*-tetradecane, 2,3-dimethylhexane, 2,4-dimethylhexane, 3-methylheptane, isooctane, cyclohexane, benzene	1	15–42	1	97
	Methylcyclohexane, perfluoromethylcyclohexane	1	16–43	2	98
	n-Perfluoroheptane	1	18–30	2	322
	Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, toluene, nitrobenzene	1	15–45	1	530
	Nitromethane	1	25	1	197
	Polyethylene terephthalate—amorphous, glassy crystalline, rubbery crystalline	1	25–130	1	415
	Poly(vinyl acetate)	To 200 mm	8–40	2	411
	Polyethylene, hydropol	1	25	1	414
	Diester, phosphate ester, dimethyl silicone, methyl phenyl silicone, paraffin base oil, aromatic base oil	34–68	24–177	1	61
	Apiezon GW oil, silicone DC 702 oil, silicone DC 200 oil	1	20–83	1	85
	Esso synthetic oil, castor oil, DC 200/200 silicone fluid, blown rapeseed oil, shell rotary vacuum-pump oil	High pressures	20–140	1	431
	Santowax R	1	233–406	1	234
	Lung tissue (blood-free homogenates)	1	37	1	89
	Pentaborane	34–100	30–150	1	67
	Liquid CH_4	25–157	90–106°K	1	229
	Liquid N_2	1–295	78–109°K	0	228
	Liquid argon	To 160 mm	84–87.5°K	2	294
	Mercury	High pressures	20–140	1	431
	Liquid H_2	2–7	16–29°K	1	505
	Aqueous solutions:				
	Solute:				
	1 *N* NaCl, LiCl, HCl, KCl, NH_4Cl, $BaCl_2$, Na_2SO_4, KI, NaBr, HNO_3, NMe_4I, NEt_4Br	1	25	1	430
	Water satd with nitromethane	1	25	1	197
	Nitromethane satd with water	1	25	1	197
	Uranyl sulfate (40–243 g/l.)	34	162–300	0	583
	Methanol, 0–4 *M* in NaI	1	30	2	99
Neon	Water	1	9–74	2	429
		1	1–15	1	327
		1	38	2	267
	Sea water	1	0–25	1	327
	n-Hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, *n*-tetradecane, 3-methylheptane, 2,3-dimethylhexane, 2,4-dimethylhexane, isooctane, cyclohexane, benzene	1	14–39	1	97
	Methylcyclohexane, perfluoromethylcyclohexane	1	16–43	2	98
	Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, toluene, nitrobenzene	1	15–55	1	530
	Nitromethane	1	25	1	197
	Poly(vinyl acetate)	To 200 mm	8–40	2	411
	Olive oil, human fat (pooled)	1	38	2	267
	Liquid argon	To 140 mm	83.9–87.5°K	2	293, 294
	1 *N* NaCl, LiCl, KI	1	25	1	430
Argon	Water	1	0–20	2	173
		1	15–25	1	197
		1	11–74	2	429
		1	25–40	2	260
		To 700	10–50	0	443
		1	3–28	2	38
		1	30	2	99
		1	2–27	2	318
		1	10–20	1	327
		1	30	1	260
		1	3–30	2	152
		1	5–25	1	40
	Water (hydrostatic pressure)	1–102	25	1	169
	Sea water	1	1–20	1	327
	Methanol	1	30	1	260
		1	30	2	99
	1-Propanol, 1-butanol, 1-pentanol, ethylene glycol	1	25–35	2	223

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Methanol, ethanol, 1-propanol, 1-butanol 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol	1	25–35	1	66
	p-Dioxane	1	5–25	1	40
	Nonpolar solvents	To 300		0	230
	n-Hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, *n*-tetradecane, 3-methylheptane, 2,3-dimethylhexane, 2,4-dimethylhexane, isooctane, cyclohexane, benzene	1	15–41	2	97
	Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, toluene, nitrobenzene	1	15–55	2	530
	Methylcyclohexane	1	−10 to 25	2	494
		1	16–43	2	98
	Toluene	1	15–30	2	494
	p-Xylene	1	30	2	95
	CCl_4	1	−20 to 10	2	494
	Perfluoromethylcyclohexane	1	5–35	2	494
		1	16–43	2	98
	n-Perfluoroheptane	1	25	2	222
	$(C_4F_9)_3N$	1	4–32	2	322
	Nitromethane	1	25	1	197
	Carbon disulfide	1	−20 to 25	2	494
		1	25	2	222
	Olive oil	1	22–37	0	360
	Paraffin wax	292–767 mm	72	1	501
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Polyethylene terephthalate—amorphous, glassy crystalline, rubbery crystalline	1	25–130	1	415
	Eel blood	1	7	1	580
	Hydrated Fe and Al oxides; soln of egg albumin, gelatin, serum, and serum albumin	1	10–40	0	567
	Liquid NH_3	25–100	0–50	2	116
		To 800	25–100	2	413
		25–100	0–25	2	117, 118
	Ammonia	0–7800	70–150	1	614
	Krypton—bulk and absorbed in layers	0–satn point	77°K	0	573
	Xenon—absorbed in layers	0–satn point	78°K	0	572
	Aqueous solutions:				
	Solute:				
	NaCl up to 3.46 *M*	1	0–20	2	173
	NaI, NaCl, NaBr, KCl, LiCl	1	20–40	2	260
	NaCl, $CaCl_2$, $MgCl_2$	1	5–90	1	422
	1 *N* NaCl, LiCl, KI	1	25	1	430
	Water–NaI soln	1	30	1	260
	Water, 0–7 *M* in NaI	1	30	2	99
	Water–ethanol mixture (X_{EtOH} = 0.015–0.25)	1	4–30	2	39
	Water satd with nitromethane	1	25	1	197
	Nitromethane satd with water	1	25	1	197
	Water–*p*-dioxane (all compositions)	1	5–25	1	40
	Nonaqueous solutions:				
	Methanol, 0–4 *M* in NaI	1	30	2	99
	Methanol soln of tetramethylammonium iodide, tetramethylammonium bromide, $CaCl_2$, NaI	1	30	1	260
	p-Xylene–*p*-dichlorobenzene (3 mixtures)	1	30	2	95
	p-Xylene–*p*-dibromobenzene (2 mixtures)	1	30	2	95
	p-Xylene-*p*-diiodobenzene (1 mixture)	1	30	2	95
Krypton	Water	1	7–75	2	429
		1	1–24	1	327
		1	30	1	582
		1	25–45	2	668
		To 41,000	100–300	1	14
	Sea water	1	0–24	1	327
	n-Hexane	1	−90 to 25	1	582
	n-Heptane, *n*-dodecane	1	25	1	582
	n-Hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, *n*-tetradecane, 3-methylheptane, 2,3-dimethylhexane, 2,4-dimethylhexane, isooctane, cyclohexane, benzene	1	16–41	2	97
	p-Xylene	1	30	2	95
	p-Xylene	1	30	1	582
	Mesitylene	1	26	1	582
	Methylcyclohexane, perfluoromethylcyclohexane	1	6–43	2	98
	Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, toluene, nitrobenzene	1	15–55	2	530
	Nitromethane	1	25	1	197
	Olive oil	1	22–37	0	360
		1	25–45	2	667
	Amsco 123-15	1	−55 to 150	1	582
	Ultrasene	1	23	1	582

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Terphenyl	1	25	1	582
	Dog fat, human fat, rat-pooled fat	1	25–45	2	667
	Aq 0–20% bovine serum albumin, 0–20% bovine hemoglobin, 0–8% bovine γ-globulin	1	37	1	434
	Aqueous solutions:				
	Solute:				
	1 *N* NaCl, LiCl, HCl, KCl, NH$_4$Cl, BaCl$_2$, Na$_2$SO$_4$, KI, KBr, KNO$_3$, HNO$_3$, NMe$_4$I, NEt$_4$Br	1	25	1	430
	0.066 *M* phosphate buffer, pH 7.0	1	25–45	2	668
	0.9% NaCl	1	25–45	2	668
	Aq soln uranyl sulfate	To 50,000	100–300	1	14
	Methanol–water (83% methanol)	1	−120 to −129	1	582
	p-Xylene–*p*-dichlorobenzene (3 mixtures)	1	30	2	95
	p-Xylene–*p*-dibromobenzene (2 mixtures)	1	30	2	95
	p-Xylene–*p*-diiodobenzene (1 mixture)	1	30	2	95
Xenon	Water	1	0–20	2	173
		1	13–72	2	429
		1	5–25	1	327
		1	30	1	582
		1	25–45	2	668
		7–21	100–300	0	583
	D$_2$O	6–14	162–300	0	583
	Sea water	1	0–25	1	327
	n-Hexane, *n*-dodecane, isooctane, benzene, cyclohexane	1	16–43	2	96
	n-Heptane	1	22	1	582
	Acetic acid	1	28	1	582
	Xylene (tech)	1	32	1	582
	p-Xylene	1	0–29	1	582
	Mesitylene	1	20	1	582
	Methylcyclohexane, perfluoromethylcyclohexane	1	16–43	2	98
	Toluene	1	24	1	582
	CCl$_4$			0	302
	Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, toluene, nitrobenzene	1	15–55	2	530
	Nitromethane	1	25	1	197
	Aniline	1	30	1	582
	Dow Corning silicone oils	1	24–95	1	582
	Ultrasene, halocarbon 437, olive oil, pine oil, Dowtherm A, Dow Corning Anti-Foam A, Koppers Emulsion K-900	1	19–32	1	582
	Amsco 123-15	1	24–150	1	582
	Olive oil	1	22–37	0	360
	Dog fat, human fat, rat-pooled fat, olive oil	1	25–45	2	667
	Aq soln human hemoglobin	1	20	1	547
	Aq 0–20% bovine serum albumin, 0–20% bovine hemoglobin, 0–8% bovine γ-globulin	1	37	1	434
	Aqueous solutions:				
	Solute:				
	1 *N* NaCl, KI	1	25	1	430
	0–2.68 *M* NaCl	1	0–20	2	173
	0.066 *M* phosphate buffer, pH 7.0	1	25–45	2	668
	0.9% NaCl	1	25–45	2	668
	Olive oil in water emulsion	1	27	1	582
	Uranyl sulfate (40 g/l.)	12–19	100–260	0	583
	Toluene (40%)–pine oil mixture	1	25	1	582
Radon	Formic acid, acetic acid, propionic acid, butyric acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, valeric acid, oleic acid	1	25–50	2	452
	Decanoic acid, undecanoic acid, acrylic acid	1	37	2	452
	Lauric acid, tridecanoic acid	1	50	2	452
	Tributyrin, triacetin, trihexanoin, linoleic acid	1	25–37	2	452
	Olive oil, olive oil (Italian)	1	25–37	2	452
	Rat fatty acids (extracted), human fat (extracted), butterfat	1	37	2	452
	Petroleum oils	Very low	Room	1	200

Elementary Gases

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
Hydrogen	Water	1	25	0	174
		1	12–71	2	428
		0–72	217	2	29
		68–204	2–335	1	588
		7–24	52–343	1	481
		To 50		0	24
		To 100	100–162	0	583
	Methanol	85–800	24–99	2	416
		10–80	0–45	2	560
	Alcohol	1	20	2	378
	2-Butanol		80–150	0	9

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Cyclohexanol	1	25–140	1	347
	Phenol	1	40–140	1	347
	Liquid methane	34–272	−157 to −101	0	36
		180–230	90–127°K	2	177
	Ethane	17–545	−184 to 24	2	653
	n-Propane	7–540	4–88	0	84
	n-Butane	20–103	24–116	1	44A
		20–545	−130 to 24	0	167
	Isobutane	34–200	38–121	2	141
	n-Hexane	48–145	35	1	527
		120–680	4–204	0	447
	n-Heptane	50–300	25–50	2	352
		1	−35 to 35	2	105
		1	35	1	374
		1	−30 to 50	2	103
		1	35	2	104
	n-Octane	1	−25 to 35	2	105
		50–300	25–50	2	352
	Octane (tech)		80–150	0	9
	n-Nonane	1	25–30	2	599
	n-Decane	20–40	40–80	1	445
	2,2,4-Trimethylpentane	1	−25 to 35	2	105
		12–342	38–150	2	141
	Ethylene	17–545	−157 to −18	2	653
	Propylene	17–545	−157 to 24	2	653
	Cyclohexane	48–145	35	1	527
		To 700	20–60	2	337
		1	25–60	1	347
	Benzene	48–145	35–73	1	527
		240–2900	25–150	2	272
		50–487	25	2	340
		1	10–45	2	103
		1	10–35	2	105
		1	25–60	1	347
	Toluene	1	−15 to 35	2	103, 105
			80–150	0	9
	m-Xylene	48–145	35	1	527
	n-Perfluoroheptane	1	−25 to 50	2	103
		1	−25 to 35	2	105
		1	25–50	2	216
	CCl_4	1	0–35	2	103, 105
	Carbon disulfide	1	−25 to 25	2	103, 105
		1	25	2	216
	Cottonseed oil, lard	1	40	1	532
	Butter oil	1	40–60	1	532
	Tetralin, olive oil		25	1	127
	2 oils (mol wt 400 and 610)	1	0–100	1	23
	Hydrocarbon mixture (av mol wt 250)	10–968	106–200	2	473
	Hydrocarbon (slack wax mol wt 345)	2–968	106–300	2	473
	Paraffin oil	1	20	2	378
	Various fats		50–220	0	619
	Poly(vinyl acetate)	To 200 mm	8–40	2	411
	Santowax R	1	241–404	1	234
	Decalin (*trans*)	1	20–140	1	347
	Hydrated Fe and Al oxides; soln of egg albumin, gelatin, serum, and serum albumin	1	10–40	0	567
	Liquid argon	10–100	87–140°K	2	630
	Liquid nitrogen	3.5–46	90–95°K	0	388
		1–900	79–109°K	2	227
		5–45	63–75°K	0	460
	Liquid diborane	0–40	113–181°K	2	265
	Liquid ammonia (nomograph)				131
	Pentaborane	34–100	30–50	1	67
	Octamethylcyclotetrasiloxane	8–21	30	1	90
	Aqueous solutions:				
	Solute:				
	$NaCl$, $LiCl$, $LaCl_3$	1	13–72	2	428
	1% gelatin in water	1	25	0	174
	Uranyl sulfate, uranyl fluoride (40–243 g/l.)	To 100	100–162	0	583
	Ammoniacal cuprous carbonate and cuprous formate solutions	To 4		0	24
	Naphtha mixture	30–85	100–200	0	299
	Isomeric dodecane mixture	34–342	93–149	2	141
	Hexene–hexane, heptene–heptane, octene–octane		80–150	0	9
	Cyclohexane–benzene mixtures	1	40	1	347
	Methane–propane mixtures	34–68	−129 to −18	0	36

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
Deuterium	D_2O	4–28	162–300	0	583
	Heptane, octane, 2,2,4-trimethylpentane, benzene, toluene, CCl_4, *n*-perfluoroheptane, CS_2	1	−35 to 35	2	105
	n-Heptane, *n*-octane	50–300	25–50	2	352
	Liquid argon	10–100	87–120°K	2	630
	Liquid nitrogen	3–69	90–95°K	0	388
	KNH_2 in liquid NH_3	1	−64 to −42	1	28
Nitrogen	Water	34–204	0–260	1	588
		97	0–240	0	369
		1	25	2	427
		10–27	260–316	2	481
		1	12–73	2	428
		68–204	18	0	157
		1	25	2	70
		To 50		0	24
		1	Room	1	593
		11–58	30	1	578
			150–200	0	442
		1	2–27	2	318
		1	3–37	2	176
		1	30	1	260
		1	3–30	2	152
		1	38	2	266
	Water (hydrostatic pressure)	100–500	0–25	1	317
		1–102	25	1	169
	Water, N_2 isotopes in	1	2–27	2	319
	Anaerobic seawater, N_2 isotopes in	1	5–29	2	499
	1-Propanol, 1-pentanol, cyclohexanol, ethylene glycol	1	25	2	223
	Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol	1	25–35	1	66
	Methanol, ethanol, 2-propanol, 1-butanol, ethanol (95%)	1	−25 to 50	2	342
	Methanol	48–280	0–75	1	339
		10–80	0 to −45	2	560
		1	25–35	1	260
	Alcohol	1	20	2	378
	Liquid methane	100–750 mm	90°K	1	626
	Liquid propane	100–750 mm	90°K	1	626
	Butane	34–286	38	0	4
	n-Hexane	1	25	2	218
	n-Heptane	68–680	32–182	0	3
	n-Heptane, *n*-octane, *n*-nonane	1	25–35	2	599
	2,2,4-Trimethylpentane	1	20	2	23
		1	−25 to 50	2	342
	Cyclohexane	1	25	2	218
	Benzene	60–300	30–150	2	420
		27–775	25	2	340
		1	25	2	218
	Toluene	15–400	200–275	1	617
	Nonpolar solvents	To 300		0	230
	Freon-114	1–9	20–60	1	654
	n-Perfluoroheptane	1	0–50	2	218
	Perfluoromethylcyclohexane	1	25	2	218
	Perfluorodimethylcyclohexane	1	25–50	2	218
	Acetone	1	−25 to 50	2	342
	Nitromethane	1	25	1	197
	Dimethylformamide	400–900 mm	5–40	1	237
	n-Propyl nitrate	1	Room	1	13
	$(C_4F_9)_3N$	1	11–30	2	322
	Carbon disulfide	1	25	2	218
		1	6–31	2	322
	Human fat (pooled), human fat (individual), dog fat, olive oil	1	37	2	266
	Olive oil, tetralin, oleic acid, ethyl palmitate		25	1	127
	Cottonseed oil, lard	1	40	1	532
	Butter oil	1	40–60	1	532
	Paraffin oil	400–760 mm	20–82	2	378
		200–770 mm	20	1	377
	Santowax R	1	238–409	1	234
	6 oils (av mol wt 400–670)	1	0–100	2	23
	Electrical insulating oil	1	26–66	2	181
	4 crude oils	0–300	20	0	519
	4 Russian crude oils	1–300	20–100	0	518
	Baku crude oils	50–300	20–100	0	682
	Crude oils, kerosine, and gasoline	1	20–60	0	604
	Petrowax A	246–790 mm	82	1	501
	Paraffin wax	265–774 mm	76	1	501
	Polyethylene terephthalate—amorphous, glassy crystalline, rubbery crystalline	1	25–130	1	415

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Polyethylene, hydrogenated polybutadiene, and natural rubber	1	25	1	414
	4 aircraft fuels			0	183
	100 octane fuel (av mol wt 100)	1	20	2	23
	Kerosene (av mol wt 165)	1	0–20	2	23
	Kerosene (jet fuel)	1	16	2	144
	Human blood and plasma, human urine	1	37	2	176
	Blood	1	37.5	0	122
	Eel blood	1	7–20	1	580
	Hydrated Fe and Al oxides, soln of egg albumin, gelatin, serum, and serum albumin	1	10–40	0	567
	Liquid SO_2		25	0	613
	Liquid SO_2	11–35	−32 to 28	1	142
	Liquid NH_3	50–100	0–50	2	116
	Liquid NH_3 (nomograph)				131
	Liquid CO_2	50–100	15–30	0	338
	Pentaborane	34–100	30–150	1	67
	Aqueous solutions:				
	Solute:				
	NaI	1	30	1	260
	1 *N* NaCl, LiCl, KI	1	13–72	2	428
	0.5–4.0 *N* NaOH	97	0–240	0	369
	1.38 *N* in NaCl and 5.41 *N* in $CaCl_2$, 2.5–5.0 *N* $MgSO_4$, 1–5.5 *N* NaCl, 1–4.2 *N* Na_2SO_4, 1–11 *N* $CaCl_2$	12–75	30	1	578
	0.15 *M* $Zn(OAc)_2$, 0.05–0.15 *M* $Ni(OAc)_2$, 0.05–0.15 *M* $Hg(OAc)_2$, 0.03–0.15 *M* $Co(OAc)_2$, 0.05–0.15 *M* $Mn(OAc)_2$, and 0.05 *M* $Cu(OAc)_2$ in 1 *M* HOAc + 0.5 *M* NaOAc soln	1	25	2	70
	Detergent solution (hydrostatic pressure)	1–102	25	1	169
	Ammoniacal cuprous carbonate and cuprous formate soln	To 4		0	24
	NaCl, $CaCl_2$, $MgCl_2$			0	422
	Nonaqueous solutions:				
	NaI–methanol solutions	1	25–35	1	260
	Acetone + ethanol (50 vol. %), ethanol + 2,2,4-trimethylpentane (50 vol. %)	1	−25 to 50	2	342
	50% Decanol–dodecanol	400 mm	20–82	1	378
Oxygen	Water	97	0–240	0	369
		1	25	2	427
		1	20	1	539
		1	0–20	2	173
		7–21	218–343	1	481
		1	13–75	2	428
		To 100	100–163	2	482
		1	3–39	2	609
		68–136	0–330	1	686
		1	0–36	2	610
		1	25	2	11
		1	6–24	2	581
		1	2–29	2	166
		1	20	2	478
		14–23	125–200	1	14
		1	Room	1	593
		1	2–27	2	318
		1	0–35	2	231
		1	8–30	2	152
		1	5–30	2	425
		1	0.4–37	0	424
		To 200	100–290	0	583
	Water (hydrostatic pressure)	100–500	25	1	317
		1–102	0.5–25	1	169
	Water (O_2 isotopes in)	1	2–27	2	319
	Water (nomograph)	690–780 mm	0–35	0	136
	Sea water	1	2–27	2	424
		1	0–35	2	231
	Sea water (hydrostatic pressure)	1–102	25	1	169
	Saline water	1	0–40	2	611
	Ethanol	1	0–70	1	539
	Ethanol, ethanol (95%), methanol, 2-propanol, 1-butanol	1	−25 to 50	2	342
	Methanol, 1-propanol, 2-propanol, 1-butanol, ethylene glycol, glycerine, rizinusöl	1	20	1	539
	Methanol	1	20	2	478
	Alcohol	1	20	2	378
	Methyl acetate, ethyl acetate	1	20	1	539
	n-Heptane, *n*-octane	1	25–35	2	599
	n-Nonane	1	25	2	599

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	2,2,4-Trimethylpentane	1	20	1	539
		1	−25 to 50	2	342
		1	10–30	2	322
		1	20	2	22, 23
	Benzene	1	0–70	1	539
	Toluene	1	20	1	497
	p-Xylene	1	20	1	539
		1	30–80	2	187
	Xylene (tech)	1	23–100	1	497
	Carbon tetrachloride, tetrachloroethylene	1	20	1	539
	n-Perfluoroheptane	1	25	2	216
	Acetone	1	−25 to 50	2	342
	Acetone, diethyl ether, paraldehyde	1	20	1	539
	Aniline	1	20	1	539
	n-Propyl nitrate	1	Room	1	13
	$(C_4H_9)_3N$	1	6–32	2	322
	Carbon disulfide	1	25	2	216
	Methylal	1	20	1	539
	Dioxane	1	20	1	539
	Liquid paraffin, olive oil, silicone fluid (1 and 5 cs.)	1	38	1	504
	Polydimethylsiloxane oil	4–21	30	1	90
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Polyethylene terephthalate—amorphous, glassy crystalline, rubbery crystalline	1	25–130	1	415
	Petroleum ether, paraffin oil, benzol, cracked gasoline	1	20	1	539
	Paraffin wax	238–808 mm	72	1	501
	Petrowax A	290–787 mm	82	1	501
	Olive oil, tetralin		25	1	127
	100 octane (av mol wt 100)	1	20	2	23
	Kerosene (jet fuel)	1	16	2	144
	Kerosene (av mol wt 165)	1	0–20	2	23
	Ligroin, white spirit fraction, cracking gasoline	1	19	1	497
	6 oils, kerosene, 100 octane aviation fuel	1	20	2	22
	Cottonseed oil, lard	1	40	1	532
	Butter oil	1	40–60	1	532
	6 oils (av mol wt 400–670)	1	0–100	2	23
	Paraffin oil	200–770 mm	20	1	377
		1	20	2	378
	Electrical insulating oil	1	22–66	2	181
	Hydrated Fe and Al oxides; soln of egg albumin, gelatin, serum, and serum albumin	1	10–40	0	567
	Whole blood	1	Room	1	656
	Blood	1	37.5	0	122
	Eel blood	1	8–20	1	580
	Liquid Cl_2	5–12	25	2	345
	Nitric acid (100%)		25	0	579
		8–22	38–88	0	502
	Aqueous solutions:				
	Solute:				
	NaCl, LiCl, KCl, $MgCl_2$	1	0–20	2	173
	NaCl (15, 30 g/kg)	1	0–36	2	610
	NaCl, $CaCl_2$, $MgCl_2$	1	5–90	1	422
	0.5–4.0 *N* NaOH	97	0–240	0	369
	Uranyl sulfate, uranyl fluoride (40–240 g of U/l.)	170	100–290	0	583
	KOH–water solutions	1	20	2	478
	Pure NH_3 solutions, pure NH_3 + $(NH_4)_2SO_4$ solutions	10–30	110–130	1	446
	0–100 wt % H_2SO_4, 0–100 wt % H_3PO_4, 0–40 wt % KOH (25° only)	1	−30 to 25	1	235
	94% HNO_3 + 6% H_2O	8–22	38–88	0	502
	Nitric acid solutions (6–31% H_2O)		25	0	579
	Uranyl sulfate solutions (40–243 g of U/l.)	100	100–163	2	482
	Uranyl sulfate	4–102	100–300	1	14
	Cane sugar, corn sugar, levulose, dextrose, corn syrup, invert syrup	1	22	1	284
	Dextrose, sucrose, levulose, cane sugar, cerelose, bakers glucose, sweetose, puritose, invert	1	19–24	1	285
	Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, ethylene glycol, glycerine (12–100 wt % alcohol)	1	30	1	539
	1 *N* NEt_4Br	1	25	1	430
	Nonaqueous solutions:				
	Acetone + ethanol (50 vol. %)	1	−25 to 50	2	342
	2,2,4-Trimethylpentane + ethanol (50 vol. %)	1	−25 to 50	2	342
	KOH–methanol solutions	1	20	2	478
	85% HNO_3 + 15% N_2O_4	8–22	38–88	0	502
	KOH in methanol–water solutions	1	20	2	478
	Nitric acid solutions (7.5–20% N_2O_4)		25	0	579
	Nitrose and H_2SO_4 solution		19	1	612

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
Ozone	Water		20	0	297
		1	15	1	255
		1	10–39	1	490
	Chloroform		−25 to −39	1	60
	Freon 11–CCl_3F	1	20	1	386
		1	−110 to −23	1	93
	Freon 12–CCl_2F_2	1	−110 to −94	1	93
	Freon 13–$CClF_3$	1	−110	1	93
	Freon 22–$CHClF_2$	1	−110	1	93
	Freon 113–CCl_2FCClF_2	1	−23	1	93
	Freon 114–$CClF_2CClF_2$	1	−63	1	93
	H_2SO_4 (5–70%)		20	0	297
Chlorine	Water	0.06–1.0	10–25	2	645–647
	Water (nomograph)				128
	Cyclohexane	100–800 mm	10–40	1	615
	Benzene	1	10–50	2	341
		1	25–68	2	92
	Chlorobenzene	1	25–65	2	92
	n-Perfluoroheptane	1	0–25	2	219
	Hexachlorobutadiene	1	−20 to 92	1	329
	Carbon tetrachloride	2.0–2.7	40–90	2	576
	Liquid $TiCl_4$	1.5–6	20–30	2	345
	Aqueous solutions:				
	Solute:				
	0.1–4 *M* $LiClO_4$, 0.1–8 *M* $NaClO_4$	1	10–50	0	291
	NaCl (210–300 g/l.)	0.1–1	30–70	1	672
	0.1–3.0 *N* $BaCl_2$	1	10–50	0	51
	LiCl, $BaCl_2$, $SrCl_2$		10–50	0	292
	$HClO_4$ (up to 50 wt %)		0–50	0	551
Air	Water	97	0–240	0	369
			21	1	549
		1	20	2	22
		1	20	2	23
		68–238	25–65	2	157
				0	168
		1	0–30	1	42
	Ice	1	0	0	543
	Sea water (several salinities)	1	0–30	1	42
	2,2,4-Trimethylpentane	1	20	2	22, 23
	Freon 12, Freon 22	To 7	−40 to 24	1	468
	n-Propyl nitrate	1	Room	1	13
	Butter oil	1	40–60	1	532
	Cottonseed oil, lard	1	40	1	532
	6 oils (petroleum), kerosene, 100-octane aviation fuel	1	20	2	22
	2 100-octane fuels (av mol wt 100)	1	20	2	23
	Kerosene (av mol wt 165)	1	0–20	2	23
	6 oils (av mol wt 400–670)	1	0–100	2	23
	8 jet fuels (kerosene)	1	16	2	144
	2 kerosenes	1	−18 to 49	2	144
	9 heavy lube oils, 4 light lube oils, diesel fuel, 3 aviation fuels		21	1	549
	4 aircraft fuels			0	183
	Electrical insulating oil	1	22–66	2	181
	Beer			0	168
	Aqueous solutions:				
	Solute:				
	NaCl (30–309 g/l.)	68–238	25–65	2	157
	0.5–4.0 *N* NaOH	97	0–240	0	369
	Ethanol (4%)			0	168
	Acetone (satd with C_2H_2)	1	0–40	0	69
	Compound Gases				
Methane	Water	1	25	2	427
		1	0–20	2	173
		20–660	25	1	120
		20–680	25–171	2	121
		1	2–40	2	94
		1	12–75	2	428
		1	18–37	2	358
		11–51	25–30	1	153
		1	25	1	400
		1	5–45	1	640
		1	Room	1	401
	Water (nomograph)	7–815	10–38	0	139
	Methanol, ethanol, cyclohexanol	1	18–37	2	358
	Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol	1	25–35	1	66

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Methanol		−50 to 20	0	46
		40	−25 to −60	2	560
	Propane	7–98	−115 to 0	2	5
	n-Hexane	1	18–37	2	358
		41–198	38–104	2	542
	n-Heptane	1	0–21	2	461
	n-Octane	1	8–35	2	461
	n-Dodecane	1	0–32	2	461
	2,2,4-Trimethylpentane	1	3–33	2	461
	Cyclohexane	41–198	38–104	2	541
		1	18–37	2	358
	n-Decane	14–68	−29 to 4	2	330
		0–238	21–121	0	520
	Benzene	103–350	100	2	540
		30–150	100–250	1	273
		7–326	66	0	160
		1	7–21	2	461
		1	18–37	2	358
	Toluene	7–360	66	0	160
		1	5–28	2	461
	Xylene	1	3–30	2	461
	n-Perfluoroheptane	1	18–30	2	322
	Acetone	1	18–37	2	358
	Dichloroethyl ether, ethylene glycol monoethyl ether		30–70	0	175
	Furfural		30–70	0	175
	Dimethylformamide	200–900 mm	5–40	1	237
	Nitrobenzene		30–70	0	175
		0.1–35 mm	5–50	1	145
	Carbon disulfide	1	15–35	2	322
	Ethyl Cellosolve, chlorex, PFMC-4F, paraffin oil	0.1–35 mm	5–50	1	145
	Crude oils, kerosene, and gasoline	1	20–60	0	604
	Surakhany crude oil	Up to 300	20–70	0	308
	Petroleum	1–40	66–84	0	310
	Baku crude oils	50–300	20–100	0	682
	4 Russian crude oils	1–300	20–100	0	518
	Baku and American crude oils		40–80	0	606
	4 crude oils	0–300	20	0	519
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Polyethylene terephthalate—amorphous, glassy crystalline, rubbery crystalline	1	25–130	1	415
	Paraffinic, naphthenic, and aromatic lean oil	9–210	450	1	312
	Santowax R	1	237–407	1	234
	Paraffin wax	218–776 mm	72	1	501
	Liquid SO_2	12–34	−32 to 28	1	142
	CO_2	7–68	−49 to −54	0	149
	Aqueous solutions:				
	Solute:				
	NaCl (0–2.8 *M*)	1	0–20	2	173
	NaCl, LiCl, KI (1 *m*)	1	13–72	2	428
	NaCl, $CaCl_2$	Up to 93	4–45	0	376
	1.53 *N* NaCl + 6.0 *N* $CaCl_2$	25–51	30	1	153
	NaCl	14–64	30	1	153
	$CaCl_2$	11–74	25–30	1	153
	NaCl, $CaCl_2$, $MgCl_2$	1	5–90	1	422
	4.9 *M* guanidinium chloride	1	5–45	1	640
	7 *M* urea	1	5–45	1	640
Ethane	Water	1	25	2	427
		4–680	38–171	1	119
		1	0–20	2	173
		4–82	38–171	1	120
		1	2–40	2	94
		1	12–72	2	428
		1–16	0	1	123
		1	10–35	2	659
		1	15–35	2	660
		1	25	1	400
		1	5–45	1	640
		1	Room	1	401
	Methanol, ethanol, 1-butanol	1	25	2	223
	1-Propanol, 1-pentanol, cyclohexanol, ethylene glycol	1	25–35	2	223
	Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol	1	25–35	1	66
	n-Heptane, *n*-nonane, *n*-octane	1	25	2	599
	2,2,4-Trimethylpentane	1	14–32	2	322
	Cyclohexane	7–68	10–66	0	301
	n-Perfluoroheptane	1	25	2	222, 599

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Benzene	14–97	0–290	1	300
	Dichloroethyl ether, ethylene glycol monoethyl ether		30–70	0	175
	Furfural		30–70	0	175
	$(C_4F_9)_3N$	1	14–31	2	322
	Nitrobenzene		30–70	0	175
	Carbon disulfide	1	25	2	222
	Polyethylene, hydropo	1	25	1	414
	Polyethylene terephthalate	1	25	1	415
	4 aircraft fuels			0	183
	Paraffinic, naphthenic, and aromatic lean oil	9–210	29	1	312
	4 Surakhany crude oils	0–100	56–86	0	307
	Petroleum	1–40	66–84	0	310
	4 Russian crude oils	1–300	20–100	0	518
	Baku and American crude oils		40–80	0	606
	Lysozyme (10%), hemoglobin (5%), serum albumin solution (5%)	1	10–35	2	659
	Aqueous solutions:				
	Solute:				
	0–3 *M* NaCl	1	0–20	2	173
	1 *m* NaCl, LiCl, KI	1	12–72	2	428
	0.5–1.5 *M* $CaCl_2$, 0.5–2.0 *M* NaCl	1–16	0	1	123
	Sodium lauryl sulfate (1.8%)	1	10–35	2	659
	Sodium dodecyl sulfate	1	15–35	2	660
	7 *M* urea, 4.9 *M* guanidinium chloride	1	5–45	1	640
Propane	Water	1	12–74	2	428
		1	20–30	2	94
		0–26	12–149	0	324
		1–35	16–138	2	20
		1	10–35	2	659
		1	15–35	2	660
		1	25	1	400
		1	5–45	1	640
		1	Room	1	401
	Water (nomograph)	1–7	16–54	0	138
	Methanol	30–760 mm	0–50	2	344
	Ethanol	12–760 mm	0–50	2	343
	2-Propanol	8–760 mm	0–50	2	344
	n-Hexane, *n*-octane	1	25	2	600
	Benzene	10–50	150–210	2	273
		1	25	2	600
	n-Perfluoroheptane	1	25	2	600
	Dichloroethyl ether, ethylene glycol monoethyl ether		30–70	0	175
	Furfural		30–70	0	175
	1,4-Dioxane	1	25	2	600
	Nitrobenzene		30–70	0	175
	Paraffinic, naphthenic, and aromatic lean oil	8–204	29	1	312
	3 Surakhany crude oils	0–25	40–85	0	307
	Petroleum	1–40	66–84	0	310
	Paraffin oil			0	377
	4 Russian crude oils	1–300	20–100	0	518
	Baku crude oils	50–300	20–100	0	682
	Baku and American crude oils		40–80	0	606
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Bovine serum albumin solution (5%), hemoglobin (5%), lysozyme (10%)	1	10–35	2	659
	Aqueous solutions:				
	Solute:				
	NaCl, LiCl, KI (1 *m*)	1	12–72	2	428
	NaCl (0–24 wt %)	0.1–1	0–20	2	621
	Sodium lauryl sulfate (1.8%)	1	10–35	2	659
	Sodium dodecyl sulfate	1	15–35	2	660
	7 *M* urea	1	5–45	1	640
	4.9 *M* guanidinium chloride	1	5–45	1	640
Cyclopropane	Water	1	35	2	364
		1	25–38	2	268
		1–41	21–104	2	269
		1	25–34	2	601
	n-Hexane	1	25	2	601
	Benzene	1	25	2	601
	n-Perfluoroheptane	1	25	2	601
	Dioxane	1	25	2	601
	Dog hemoglobin (9.5%), homogenized rabbit muscle, homogenized rabbit liver	1	35	2	364
	Olive oil, pooled rat fat	1	25–38	2	52
	Blood	1	27–37	2	479
	Bovine whole blood, plasma, olive oil	1	25–38	2	268

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Aqueous solutions:				
	Solute:				
	NaCl (0.9 wt %), Na phosphate buffer	1	35	2	364
	Bovine serum albumin (10%)	1	35	2	364
	Bovine serum albumin (0–25%)	1	37	2	179
	Bovine serum albumin, hemoglobin, γ-globulin, β-globulin	1	37	1	434
n-Butane	Water	1	20–30	1	94
		1	11–76	2	428
		To 200	40–100	0	440
		1	10–35	2	659
		1	15–35	2	660
		1	25	1	400
		1	5–45	1	640
		1	Room	1	401
	Methanol	200–760 mm	25–50	2	344
	Ethanol	60–740 mm	25–50	2	343
	2-Propanol	80–760 mm	25–50	2	344
	Paraffinic, naphthenic, and aromatic lean oil	9–210	29	1	312
	Aqueous solutions:				
	Solute:				
	NaCl, KCl, LiCl, HCl, KI, $BaCl_2$, $LaCl_3$ (1 *m*)	1	11–76	2	428
	NaCl (0–24 wt %)	0.1–1	0–20	2	621
	4.9 *M* guanidinium chloride	1	5–45	1	640
	7 *M* urea	1	5–45	1	640
	1 *N* KBr, NEt_4Br	1	25	1	430
	Hemoglobin (5%), bovine serum albumin solution, Na lauryl sulfate (1.8%), lysozyme (10%)	1	10–35	2	659
	Bovine serum albumin solutions with 0.15 *M* NaCl	0.2–1	25	0	661
	Bovine serum albumin (5%)	1	25	1	641
	Sodium dodecyl sulfate	1	15–35	2	660
Isobutane	Water	1	25	1	400
		1	5–45	1	640
		1	Room	1	401
	Methanol	364–760 mm	25–50	2	344
	Ethanol	23–760 mm	10–50	2	343
	2-Propanol	355–760 mm	25–50	2	344
	Dichloroethyl ether, ethylene glycol monoethyl ether		30–70	0	175
	Furfural		30–70	0	175
	Nitrobenzene		30–70	0	175
	Aqueous solutions:				
	Solute:				
	7 *M* urea	1	5–45	1	640
	4.9 *M* guanidinium chloride	1	5–45	1	640
	1% potassium oleate	100–650 mm	25	1	402
n-Pentane	Water	1	15–35	2	660
	Paraffinic, naphthenic, and aromatic lean oil	9–210	29	1	312
	Bovine serum albumin in 0.15 *M* NaCl	1	25	1	661
	Sodium dodecyl sulfate	1	15–35	2	660
Neopentane	Water	1	15–45	1	640
		1	Room	1	401
	4.9 *M* guanidinium chloride	1	15–45	1	640
	7 *M* urea	1	15–45	1	640
Ethene	Water	1	25	2	427
		4.5–520	35–100	2	68
		1	14–73	2	428
		1	30	2	260
		To 193	25–150	0	253
		1–34	35–121	2	140
		1	Room	1	401
	Methanol		−50 to 20	0	46
		To 193	25–150	0	564
		1–18	−56 to −10	2	563
		1	−70 to 20	1	624
	Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol	1	25–35	1	66
	n-Decane	20–40	40–80	2	445
	n-Hexane, cyclohexane	To 120	30–150	0	683
	n-Hexane	1	−30	1	362
	n-Heptane	1	−60 to −20	1	362
	Methylcyclohexane	1	−60 to −50	1	362
	Benzene	40–190	25–150	0	252
		To 193	25–150	0	564
		To 120	30–150	0	683

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Toluene	1–18	−45 to −25	2	253
		1	−60 to −30	1	362
	m-Xylene	1	−70 to 20	1	624
	Chloroform	1	−30	1	362
	Carbon tetrachloride	1	−20	1	362
	Dichloroethane	1	−70 to 20	1	624
	Acetone	1–18	−45 to −25	2	253
		1	−30	1	362
		1	−70 to 20	1	624
	Methyl ethyl ketone	3–18	−25 to −45	2	564
	Diethyl ether	1	−70 to 20	1	624
	Methyl acetate	1	−70 to 20	1	624
	Tetrahydrofuran	To 193	25–150	0	253
	Dimethylformamide	1	0 to −45	2	562
		1	−70 to 20	1	624
	Methylpyrrolidone	1	−70 to 20	1	624
	Baku crude oils	50–300	20–100	0	682
	4 Russian crude oils	1–300	20–100	0	518
	4 crude oils	0–300	20	0	519
	Diethyl sulfate	50–1300 mm	0–80	2	608
	Aqueous solutions:				
	Solute:				
	KCl, $AgNO_3$	1	30	2	260
	1 *N* NaCl, LiCl, KI, $LaCl_3$	1	13–72	2	428
	N-Methylpyrrolidone with 0–60 mole % H_2O	0–800 mm	0–45	1	565
	0.5 mole fraction of toluene–heptane, toluene–chloroform, toluene–methylcyclohexane, *n*-heptane–carbon tetrachloride, acetone–chloroform, acetone–*n*-hexane	1	−60 to −20	1	362
Propene	Water	400 mm	25	0	402
		500–700 mm	25	0	403
		1–34	21–104	2	21
		1	Room	1	401
	Methanol		−47 to 20	1	622
	Dimethylformamide	1	0 to −45	2	562
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Aqueous solutions:				
	Solute:				
	0–15% potassium oleate	400 mm	25	0	402
	21 detergent solutions	500–700 mm	25	0	403
	0.5–5% K_2CO_3	500–700 mm	25	0	403
	Emulsifiers			1	674
	N-Methylpyrrolidone with 0–60 mole % H_2O	0–800 mm	0–45	1	565
Propadiene	Polyethylene, hydropol, and natural rubber	1	25	1	414
2-Methylpropene	Water	1	0–70	1	303
		1	Room	1	401
	Dichloroethyl ether, ethylene glycol monoethyl ether, furfural, nitrobenzene		30–70	0	175
	Dinonyl phthalate	73–740 mm	0–100	1	262
	Triisobutylaluminum	1	10–50	1	477
	5% aq NaCl	1	−5 to 0	1	303
	Emulsifiers, aq soln			1	674
1-Butene	Water	2–68	38–143	1	74
		1	Room	1	401
1,3-Butadiene	Water	100–500 mm	25	2	402
		1	25	1	507
		To 19	38–104	1	493
		1	Room	1	401
	1% potassium oleate, aq	100–500 mm	25	2	402
	1–4% Hyamine 1622, aq	1	25	1	507
Pentene	Paraffin oil			0	377
Acetylene	Water	1	20	0	387
		5–39	1–30	1	251
		To 29	0–30	0	315
		1	0–70	0	188
		To 39	20–45	0	253
	Methanol	1–29	0–30	2	313
		1	1–30	1	591
		To 29	0–30	0	315
			25–60	0	533
		1	−75 to −25	2	423
		3–14	−20 to 20	1	513
		To 39	20–45	0	253
		1	"Low temp"	0	623

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Ethanol	1	−75 to −25	2	423
		1	18	0	109
	Methanol, 1-butanol, allyl alcohol, ethylene glycol	1	25	0	259A
	Diacetone alcohol	To 11	25	0	259A
	Acetic acid	1	18	0	109
	Methyl acetate	1	"Low temp"	0	623
	Ethyl acetate	To 11	25	0	259A
		1	−75 to 45	1	55
			25–60	0	533
	Ethyl acetoacetate	To 25	25	0	259A
	Trimethyl orthoacetate	1	0	2	632
	Vinyl acetate	1	0–40	2	239
	Trimethyl orthoformate	1	0	2	632
	Diethyl oxalate	602 mm	25	0	259A
	Triethyl phosphate		25–60	0	533
	Ethyl acetate, ethyl formate, methyl acetate, methyl formate, isoamyl acetate, isoamyl formate	1	−10	0	109
	Tetramethyldiamidophosphonyl fluoride, methyl phosphite, methyl orthoacetate, trimethyl mercaptophosphate, methyl borate, methylene diacetate, ethyl perfluorobutyrate, ethyl orthoformate	1	25	1	410
	n-Hexane	1	−25	1	362
	n-Hexane, *n*-octane	3–14	−20 to 20	1	513
	Cyclohexane	1	3	0	109
	Dicyclopentadiene	721 mm	25	0	259A
	Benzene	5–29	10–40	2	314
		To 29	0–30	0	315
		To 39	20–45	0	253
		1	20–60	2	628
		1	4	0	109
	Toluene	3–14	−20 to 20	1	513
		1	20–90	2	628
		1	−30 to 25	1	362
	m-Xylene	3–14	−20 to 20	1	513
		1	"Low temp"	0	623
	p-Xylene	1	20–120	2	628
	Chloroform	3–14	−20 to 20	1	513
		1	−30	1	362
	Dichloroethane	770 mm	25	0	259A
		1	"Low temp"	0	623
	Ethyl bromide, ethyl iodide	256–648 mm	19–25	2	198B
	Acetone	1	−70 to 40	0	69
		1	20–39	0	387
		1.4–30	3–40	2	259
		1	−75 to 45	1	55
			25–60	0	533
		1	−80 to −40	1	616
		1	"Low temp'	0	623
		1	−25	1	362
		1–12	0–15	0	109
	Butyrolactone	To 25	25	0	259A
			25–60	0	533
	Tetrahydrofurfuryl methyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, diethylene glycol dibutyl ether, diethylene glycol di-*t*-butyl ether, di-*n*-hexyl ether	3.5–14	−20 to 20	1	515
	Diethyl ether	1	−75 to −25	2	423
		1	"Low temp"	0	623
	Ethylene glycol monomethyl ether	1	−75 to 45	1	55
	Glyoxol tetramethyl acetal, diethyl oxalate diethyl acetal	1	25	1	410
	Acetaldehyde	1	−75 to 0	2	57
	Acetal, methylal., acetaldehyde	1	−10	0	109
	Dimethylacetamide	To 16	25	0	259A
			25–60	0	533
	Dimethylformamide	1	"Low temp"	0	623
		1	20–39	0	387
		To 25	15–40	0	259A
		200–900 mm	5–40	1	237
		3.5–14	−20 to 30	1	514
		0.13–1	−50 to 25	2	562
		1	25	1	362
	1-Methylpyrrolidone	750 mm	20	1	375
	N-Methyl-2-pyrrolidinone	1	−35 to 20	1	155
	N-Methylpyrrolidone	To 11	15–40	0	259A
	1,5-Dimethylpyrrolidone	3.5–14	−20 to 30	1	514
	Methylpyrrolidone	1	"Low temp"	0	623

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp °C	Measurement value (see section VI)	Ref
	Tetramethylurea	530–720 mm	15–40	0	259A
			25–60	0	533
	2-Methyl-5-ethylpyridine	3.5–14	−20 to 30	1	514
	Hexamethylphosphoric triamide	1	30–37	2	603
	Hexamethylphosphorous triamide		25–60	0	533
	Aniline, dimethylaniline, nitrobenzene	1	4	0	109
	Acetylpyrrolidine, formylpyrrolidine, N-nitrosopyrrolidine, hexamethylphosphoramide, tritetramethylenephosphoramide	1	25	1	410
	Dimethyl sulfoxide	1	15	1	575
				0	574
		3.5–14	−20 to 30	1	514
	Dimethyl sulfoxide, tetramethylene sulfoxide	1	25	1	410
	"Solvenon"	550 mm	25	0	259A
	Dioxane	1	20	0	387
		609 mm	25	0	259A
	Methylnaphthodioxane, ethylene oxide, 2-methyl-2-methoxy-1,3-dioxane, dioxane (satd with trioxane)	1	25	1	410
	Tetrahydrofuran	583 mm	25	0	259A
		To 29	0–30	0	315
		1–25	0–30	1	313
		1	−75 to 45	1	55
		To 39	20–45	0	253
	Mesityl oxide	To 11	25	0	259A
	1,1,3,3-Tetramethoxypropane	3.5–14	−20 to 20	1	515
	Morpholine, N-formylmorpholine	3.5–14	−20 to 30	1	514
	21 solvents	3.5–14	−20 to 20	1	516
	Blood, human and animal	1	37	2	486
	Lung tissue (blood-free homogenates)	1	37	1	89
	Hydrated Fe and Al oxides, soln of egg albumin, gelatin, serum, and serum albumin	1	10–40	0	567
	Liquid NH_3	1	−50 to −74	1	56
	Aqueous solutions:				
	Solute:				
	H_2SO_4, Li_2SO_4, LiCl, $NaNO_3$, NaCl, K_2SO_4, KNO_3, KCl, KBr, NH_4Cl, $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2, $MgSO_4$, $ZnSO_4$, $CdSO_4$, $MnSO_4$, $FeSO_4 + H_2SO_4$, $NiSO_4$, $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, and $Fe_2(SO_4)_3 + H_2SO_4$	1	0–70	0	188
	Dimethylformamide–water (0–100%), acetone–water (0–100%), dioxane–water (0–100%)	1	20	0	387
	Dimethylformamide (with 0–23% H_2O)	100–400 mm	25–140	1	72
	Methanol (with 0.05% H_2O)	To 1	10–78	1	71
	N-Methylpyrrolidone with 0–60 mole % H_2O	0–800 mm	0–45	1	565
	Nonaqueous solutions:				
	Potassium methylate (25%) in methanol	1	23–50	1	591
	Dimethylformamide with 5.4 g NaI/100 g	1	20–39	0	387
	Acetone with 13–30 g of NaI/100 g	1	20–39	0	387
	Dimethylformamide–dioxane (0–100%)	1	20	0	387
	Acetone–*n*-hexane (0.5 mole fraction)	1	−25	1	362
	Acetone–chloroform, toluene–chloroform (0.5 mole fraction mixtures)	1	−30	1	362
	Toluene–dimethylformamide (0.5 mole fraction)	1	25	1	362
	Mixtures of $CHCl_3$, H_2O, MeOH, or diethylene glycol dimethyl ether with dimethylformamide, dimethyl sulfoxide, or ethylene glycol dimethyl ether	3–13	0–10	1	517
Propyne	Water	To 14	21–104	2	270
		1	0–60	1	571
		1	Room	1	401
	Methanol	1	0–60	1	571
	Aqueous solutions:				
	Solute:				
	3 wt % NH_4OH	1	0–60	1	571
	Methanol (with 0.05% H_2O)	1	−70 to 20	1	71
	Dimethylformamide (with 0–23% H_2O)	100–400 mm	25–140	1	72
1-Butyne	Water	1	0–60	1	571
		1	Room	1	401
	Methanol	1	0–60	1	571
	3 wt % NaOH, 0.3–10 wt % NH_4OH, 20–25 wt % NaCl	1	0–60	1	571
3-Buten-1-yne	Water	1	0–60	1	571
	Methanol	1	0–60	1	571
	Benzene	1	20–60	2	629
	Toluene	1	20–90	2	629
	p-Xylene	1	20–120	2	629
	2-Chloro-1,3-butadiene	1	10–50	1	277

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Aqueous solutions:				
	Dimethylformamide (0–23% in H_2O)	100–400 mm	25–140	1	72
	Methanol (with 0.05% H_2O)	To 1	20 to −70	1	71
	3 wt % NH_4OH	1	0–60	1	571
Diacetylene	Methanol (with 0.05% H_2O)	To 1	20 to −70	1	71
	Dimethylformamide (with 0–23% H_2O)	100–400 mm	25–140	1	72
Carbon tetrafluoride (Freon-14)	Water	To 8	25–75	1	469
		1	7–39	2	429
	Isooctane, *n*-heptane, cyclohexane, benzene	1	5–36	2	15
	Perfluoromethylcyclohexane	1	−11 to 40	2	495
	CCl_2FCClF_2	1	5–35	2	15
Chlorotrifluoromethane (Freon-13)	Water		10–59	2	62
		To 25	25–75	1	469
Dichlorodifluoromethane (Freon-12)	Water	To 8	25–75	1	469
	Carbitol acetate, carbitol methoxyacetate, 4-methyl-2-pentanol acetate	3.5	32	0	677
	Trichlorobenzene	3.5	32	0	677
	Carbitol ethyl ether, dichloroisopropyl ether, γ,γ′-dichloro-*n*-propyl ether, diethyl ether of ethylene glycol	3.5	32	0	677
	2,3-Di-β′-ethoxy-β-ethoxydioxane	3.5	32	0	677
	α-Fluoronaphthalene	3.5	32	0	677
	30 solvents (alcohols, esters, acids, ethers, aldehydes, ketones, nitrogen compounds, 2 hydrocarbons, and 2 bromides)	3.5	32	2	108
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	3.5	32	2	678
Trichlorofluoromethane (Freon-11)	Diethyl ether of tetraethylene glycol	364 mm	32	0	677
	Carbitol acetate	364 mm	32	0	677
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	0.48	32	2	678
	29 solvents (alcohols, ethers, esters, aldehydes, ketones, nitrogen compounds, 2 hydrocarbons, and 2 bromides)	0.48	32	2	108
Chloroform	Ethanol	1.0–1.6 mm	25–35	1	27
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	0.11	32	2	678
	Acetone	0.7–1.2 mm	25–35	1	27
	Tetraethylene glycol dimethyl ether	1	3	2	395
	Olive oil	20–70 mm	20	1	383
Dichlorofluoromethane (Freon-21)	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	0.85	32	2	678
	Diethyl adipate, ethyl laurate, diethyl oxalate	To 1.5	38–107	2	7
	Tetraethylene glycol dimethyl ether	0.84	3	2	395
		1	27–90	2	399
		To 1	38–107	2	7
	Triethylene glycol dimethyl ether	To 7	20–101	2	7
	N,N-Dimethylformamide	To 1	38–107	2	7
	N,N-Dimethylacetamide	To 19	20–101	2	7
	Caprylonitrile, succinonitrile, glutaronitrile, adiponitrile, sebaconitrile	0.85	32	2	110
	44 solvents (alcohols, ethers, acids, esters, amines, amides, aldehydes, ketones, and oximes)	0.6–1	32	0	106
	78 solvents (esters, ethers, glycols, and others)	638 mm	32	0	677
	82 solvents (esters, glycols, ethers, amines, amides, and others)	0.85	32	0	678
Chlorodifluoromethane (Freon-22)	Water	To 12	25–75	1	469
			10–79	2	62
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	5.6	32	2	678
	Tetraethylene glycol dimethyl ether	5.5	3	2	395
		To 21	28–177	2	399
		To 2	38–107	2	7
	N,N-Dimethylformamide	To 2	38–107	2	7
Trifluoromethane (Freon-23)	Water	To 24	25–75	0	469
Dichloromethane	Diethyl ether of tetraethylene glycol	181 mm	32	0	677
	Tetraethylene glycol of dimethyl ether	0.23	32	2	395
	Carbitol acetate, cellosolve acetate	181 mm	32	0	677
	Ethyl ether of diethylene glycol acetate, diethyl ether of diethylene glycol, dimethyl ether of tetraethylene glycol	0.23	32	2	678
	Caprylonitrile, benzonitrile, succinonitrile, glutaronitrile, adiponitrile, sebaconitrile	0.23	32	2	110

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	35 solvents (alcohols, ethers, acids, esters, amines, amides, oximes, aldehydes, and ketones)	0.23	32	0	107
Chlorofluoromethane	Water		10–79	2	62
	Tetraethylene glycol dimethyl ether	1.7	3	2	395
		1.5–9	35–177	2	399
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	1.7	32	2	678
Bromomethane	Water	To 950 mm	0–77	0	224
		To 1	29–40	2	592
		1	10–32	2	198
	D_2O	To 1	29–40	2	592
	Pineapple, mango, and papaya juice	1	18–32	1	198
Chloromethane	Water	500 mm	20	2	390
		To 950 mm	0–77	0	224
			10–59	2	62
		To 1	29–40	2	592
	D_2O	To 1	29–40	2	592
	Ethanol	500 mm	20	2	390
	Benzene	500 mm	20	2	390
	Carbon tetrachloride	100–760 mm	−10 to 20	0	288
		500 mm	20	2	390
	Dichloroethane	100–760 mm	−10 to 20	0	288
	Ethyl ether of diethylene glycol acetate, dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol	2.9	32	2	678
	Acetic acid (glacial)	500 mm	20	2	390
	Polyethylene	1	25	1	414
	63 solvents (esters, glycols, ethers, substituted benzenes and naphthalenes, and others)	3	32	0	677
Fluoromethane	Water	To 950 mm	0–77	2	224
		To 1	29–40	2	592
	D_2O	To 1	29–40	2	592
Iodomethane	Water	To 950 mm	0–77	2	224
		To 1	29–40	2	592
	D_2O	To 1	29–40	2	592
Chloroethane	Carbon tetrachloride, dichloromethane	100–760 mm	−10 to 20	0	288
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	0.74	32	2	678
	1,1,2,2-Tetrachloroethane, dimethyl ether and diethyl ether of tetraethylene glycol, dimethyl ether of triethylene glycol, carbitol ethyl ether, carbitol acetate, butyl carbitol acetate diethylene glycol diacetate	557 mm	32	0	677
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon-113)	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	0.18	32	2	678
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)	Carbitol acetate	786 mm	32	0	677
	Dimethyl ether of tetraethylene glycol, diethyl ether of diethylene glycol, ethyl ether of diethylene glycol acetate	1	32	2	678
1-Chloro-1,1,2,2-tetrafluoroethane	Tetraethylene glycol dimethyl ether	To 8	35–177	2	399
1-Chloro-1,1,2,2,2-pentafluorethane (Freon-115)	Water	To 8	25–75	1	469
1,1,2,2-Tetrafluoroethane	Tetraethylene glycol dimethyl ether	To 5	27–86	2	399
Vinyl chloride	Methanol	1	−10 to 20	1	470
	Methylcyclohexane	1	20–50	2	382
	Tetrachloroethylene	1	−7 to 20	1	470
	1,1-Dichloroethane	1	20–50	2	382
	Tetrahydrofuran	1	20–50	2	382
	Dimethylformamide	1	20–50	2	382
	Emulsifiers, aq solutions of			0	674
	"26 different solvents"			0	531
Dichlorodifluoroethylene	Dimethyl ether of tetraethylene glycol	786 mm	32	0	677
Chlorotrifluoroethylene	Emulsifiers, aq solutions of			0	674
1,2-Epoxyethane (ethylene oxide)	Water	1	5–20	0	289
		20–700 mm	5–20	1	406
		1	12–50	2	100
	$C_{12}H_{25}OH$, $C_{12}H_{25}O(CH_2CH_2O)_5H$, $C_9H_{19}C_6H_4O(CH_2CH_2O)_5H$	0–16.4	100–150	0	436
	Dichloroethane	1	5–20	0	289

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
Ketene	Acetone			0	146
Diethyl ether	Lung tissue (blood-free homogenates)	1	37	1	89
Carbon monoxide	Methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl alcohols	1	25–50	2	215
	Alcohol	1	20	2	378
	n-Propyl acetate	1	25	2	221
	n-Heptane	1	25	2	216
	Hydrocarbon (slack wax, av mol wt 345)	1–10 (Kp/cm^2)	106–300	2	473
	Paraffin oil	1	20	2	378
	Various hydrocarbons			0	9
	Benzene	1	25	2	216
	Toluene	1	25	2	221
	1,2-Dibromoethane	1	25	2	221
	n-Perfluoroheptane	1	25	2	216
	Aniline, propionitrile, benzyl cyanide, pyridine, nitrobenzene	1	25	2	221
	Dimethylformamide	600–900 mm	5–40	1	237
	Polyethylene, hydropol, natural rubber	1	25	1	414
	Carbon disulfide	1	25	2	216
	Ammoniacal cuprous carbonate and cuprous formate solutions	To 4		0	24
	Hydrated Fe and Al oxides; soln of egg albumin, gelatin, serum, and serum albumin	1	10–40	0	567
Carbon dioxide	Water	25–500	12–40	1	649
		16–49	20–50	1	673
		25–700	0–100	2	648
		25–700	75–120	2	487
		1	13–75	2	428
		1	25	2	217
				0	168
		1–700	0–120	0	147
		1–20	10–30	2	31
		1	20–75	1	555
				0	214
				0	191
			To 350	0	164
		100–700 mm	11.5–77	2	450
		1	37.5	1	570
		1	20–30	2	114
		16–59	177–334	2	165
		1	20–38	2	18
		5–162	114–348	1	164
		1	25–45	2	668
	Water (nomograph)				597
	Water (hydrostatic pressure)	1–102	25	1	169
	Ice		−20 to −5	0	172
	Methanol	7–70	0–75	1	339
		3–19	−29 to −50	0	46
			25–60	0	533
		100–760 mm		1	557
		High pressure	−60 to −26	1	558
		1	−70 to 20	1	625
	Ethanol	100–760 mm	Low temp	0	557
	Ethanol, 95%	1	2–62	0	503
	Alcohol	1	20	2	378
	Propanol, 2-propanol, butanol, 2-butanol, 2-methyl-1-propanol	100–760 mm	Low temp	0	557
	50:50 decanol–dodecanol	100 mm	20–82	1	378
	Cyclohexanol	1	20–48	2	35
	Oleic acid	100–450 mm	23–62	1	466
	Ethyl acetate		25–60	0	533
		3–15	−45 to −25	2	559
		1	−75 to 45	1	55
	n-Propyl acetate	1	25	2	221
	Methyl acetate	1	25	2	221
	Ethyl stearate	100–600 mm	34–74	1	466
	n-Pentane	1.7–75	38	1	476
	n-Heptane, cyclohexane	1	25	2	217
	Oils and kerosenes	760 mm	0–20	2	23
	Paraffin oil	100–760 mm	20–82	2	378
		200–750 mm	20	1	377
	Paraffin wax	258–753 mm	72	1	501
	Baku crude oils	50–300	20–100	0	682
	Crude oils, kerosene, gasoline	1	20–60	0	604
	Russian crude oils	1–300	20–100	0	518

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Diesel fuels and cracked gas oils	3–40	25–50	1	368
	Baku and American crude oils		40–80	0	606
	Slack waxes	1–10 (Kp/cm^2)	106–300	2	473
	Mineral oil	1	20–48	2	35
	Benzene	10–95	30–60	1	634
		1	20–35	2	217
	Toluene	1	25	2	221
		1	−80 to 0	1	651
		3–15	−45 to −25	2	559
	n-Perfluoroheptane	1	25	2	217
		1	19–30	2	322
	$(C_4F_9)_3N$	1	4–31	2	322
	Hexachlorobutadiene	1	−11 to 55	1	329
	Carbon disulfide	1	8–33	2	322
	Methylene chloride	1–20	21	2	79
		3–20	38–54	1	631
	Chloroform	1	25	2	221
	Carbon tetrachloride	1	25	2	217
	1,2-Dibromoethane	1	25	2	221
	Ethylene bromide, propylene chlorobromide	1	20–48	1	35
	Chlorobenzene	1	25	2	221
	Acetone	1	25	2	221
		1	−75 to 45	1	55
			25–60	0	533
	Methyl ethyl ketone	3–15	−45 to −25	2	559
	Butyrolactone		25–60	0	533
	Diethyl ether	740 mm	24	2	412
	Ethylene glycol monomethyl ether	1	−75 to 45	1	55
	Acetaldehyde	1	−75 to −25	2	57
	Benzylcyanide, propionitrile	1	25	2	221
	Aniline	1	25	2	221
	Pyridine	1	25	2	221
	Dimethylformamide	1	−45 to 0	2	562
		1	−70 to 20	1	625
		200–900 mm	5 to 40	1	237
	Dimethylacetamide		25–60	0	533
	Hexamethylphosphorous triamide		25–60	0	533
	Hexamethylphosphoric triamide	1	37	1	603
	Methylpyrrolidone	1	−70 to 20	1	625
	Nitrobenzene	1	25	2	221
	Tetrahydrofuran	1	−75 to 45	1	55
	Triethyl phosphate		25–60	0	533
	Tetramethylurea		25–60	0	533
	Polyethylene tetraphthalate	1–12	25–130	1	415
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Carbon disulfide	1	25	2	217
	Butteroil, cottonseed oil, lard	1	40–60	1	532
	Dog fat, human fat, rat-pooled fat	1	25–45	2	667
	Olive oil	1	25–45	2	667
	Whole blood	1	Room	2	656
	Cerebrospinal fluid	1	37.5	1	570
	Homogenized brain tissue (of cats)	1	37.5	1	570
	Human serum	1	15–38	2	18
	Blood	1	37.5	0	122
	Ammonia, liquid	1	−74 to −50	1	56
	Chlorine, liquid	0.8–6.5	0–25	1	345
	HCN, liquid		−5 to 10	0	488
	Aqueous solutions:				
	10, 50, 95% alcohol	1	2–62	0	503
	Wine			0	2
	4% ethanol, beer			0	168
	Aqueous sucrose and citric acid soln			0	379
	Papaw juice		25	0	363
	Hydrated Fe and Al oxides, aqueous egg albumin, gelatin, serum	1	10–40	0	567
	Aerosol solution (15%)	1	25	2	217
	Dimethylformamide (0–23% water)	100–400 mm	25–140	1	72
	N-Methylpyrrolidone (0–60 mole % water)	0–800 mm	0–45	1	565
	Monoethanolamine (15%)	0.5–6980 mm	40–140	2	283
	Mono- and triethanolamine (0.5–5 *N*)	To 40	25–75	0	381
	Mono-, di-, and triethanolamine (3.6–3.9 *N*)	7–445 mm	50	0	569
	Mono-, di-, and triethanolamine	10–760 mm	50	0	568
	2.5, 5.0 *M* HF	1	20–30	2	114
	0.01 *N* HCl	1	37.5	1	570
	As_2O_3–As_2O_5–HBr soln		20–25	0	49
	9–84 wt % H_2SO_4	1	19–76	1	555
	0.1 *N* lactic acid	1	37.5	1	570

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	0.066 *M* phosphate buffer	1	25–45	2	668
	0.5–2.0 *M* NaCl	45–88	172–330	2	165
	0.9% NaCl soln	1	25–45	2	668
	0.16 *M* NaCl soln	1	37.5	1	570
	Na_2SO_4–H_2SO_4 soln	1	25–65	0	556
	K_2SO_4, K_2CO_3, K_2CO_3–$KHCO_3$, KOH			0	214
	10, 20, 30% $CaCl_2$ soln	25–700	75–120	2	487
	KCl, NaCl, KNO_3, $Mg(NO_3)_2$, $NaNO_2$, $MgSO_4$, Na_2SO_4	1	0–40	2	391
	NaOH–Na_2CO_3	0.05–1.0	18	2	618
	Glycerol in water, glycerol and sulfuric acid, ethylene glycol, β,β-dihydroxyethyl ether, tetrahydrofurfuryl alcohol, dioxane	1	25	2	325
	Binary mixtures: MeOH–acetone, MeOH–$CHCl_3$, MeOH–C_6H_6, acetone–$CHCl_3$, acetone–C_6H_6, $CHCl_3$–C_6H_6	760 mm	20	2	333
Carbon oxysulfide, COS	Methanol	Satn point	−78.5 to 0	1	681
	Ethanol	1	20	2	378
	Paraffin oil	1	20	2	378
	Green, spindle, and solar oil		30–100	0	19
	Titanium tetrachloride	1	0–100	1	675
Carbon disulfide, CS_2	Water, saline, urine, whole blood, blood plasma, red cells, bile	5–90 ppm in air	37	1	409
	Methanol	Satn point	−78.5 to 0	1	681
	Ethanol, acetone	4.2–8.7 mm	25–35	2	27
	Green, spindle, and solar oil		30 to 100	0	19
Chlorine monoxide, Cl_2O	Water	1–88 mm	3.5 to 20	2	550
	Water (nomograph)				132
	Aqueous HOCl	1–11	3.5	1	508
Chlorine dioxide, ClO_2	Water		0–40	1	274
		10–150 mm	10–45	2	305
	Carbon tetrachloride	30–125 mm	20	2	305
	10–76.5% acetic acid soln	58–158 mm	20	2	305
	9.7–79.1% H_2SO_4	40–170 mm	20	2	305
Boron trifluoride, BF_3	*n*-Pentane	3–7	49–93	1	88
	Benzene, toluene	1	23–47	2	643
	Anisole, phenetole, 2,2′-dichlorodiethyl ether	1	5–170	1	389
	Nitrobenzene		5–25	0	78
	Sulfuric acid	1	5–170	1	389
	HF, liquid	0–68	24–98	2	418
Diborane, B_2H_6	*n*-Pentane	0.5–5	0–55	1	405
	Diethyl ether	1.5–7.7	0–60	1	163
	Tetrahydrofuran	0–4	7–50	1	163
	Dimethyl ether of diethylene glycol, di-*t*-butyl sulfide	5–315 mm	0–30	1	671
	2–5.4% $NaBH_4$ in dimethyl ether of diethylene glycol	4–300 mm	30	1	671
	Ethyl Cellosolve, 2,2′-dichlorodiethyl ether, nitrobenzene, PFM-4F, paraffin oil	0.1–35 mm	5–50	1	145
Hydrides: SiH_4, GeH_4, SnH_4, SbH_3, H_2Se	Ethyl Cellosolve, 2,2′-dichlorodiethyl ether, nitrobenzene, PFM-4F, paraffin oil	0.1–35 mm	5–50	1	145
Water vapor	Hydrocarbon slack wax (av mol wt 345)	1–10 (Kp/cm^2)	140–300	2	473
	Triethylenetetramine, tetraethylenepentamine, methylated triethylenetetramine, triacetyltrimethyltriethylenetetramine, hexamethylenediamine, N,N-dimethylacetamide, ethylene glycol, glycerol, carbitol, dimethyl ether of tetraethylene glycol, triethyl phosphate	H_2O equil point at 4.5°	32.2	0	111
Hydrogen sulfide	Water	0–200 mm	0–60	1	58
			20	0	226
	Methanol	To 0.085	−30 to 30	0	46
		Low pressure	−78.5 to 0	1	681
		15–480 mm	−78.5 to 0	1	680
	n-Pentane	6.8–88	5–170	1	491
	n-Decane	6.8–81	5–170	1	492
	Cyclohexane	100–800 mm	10–40	1	615
	Spindle, green, and solar oil		30–100	0	19
	Benzene	To 48	25–175	0	367
	Ethyl Cellosolve, chlorex, nitrobenzene, PFMC-4F, paraffin oil	0.1–35 mm	5–50	1	145
	Sulfur	1	126–444	1	180
		3.0–5.0	177–260	1	510
	15.3% Monoethanolamine in H_2O	1–840 mm	40–140	2	283
	Aq ammonia		20	0	226
	Aq phenol		20	0	226
	Aq HCl, $ZnCl_2$, and $FeCl_3$ soln			0	290

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
Hydrogen chloride	24 alcohols	1	0–18	0	202
	43 solvents (15 alcohols, 8 acids, 20 esters)	1	2–67	2	203
	25 solvents (19 ethers, 6 glycols)	1	0–60	2	212
	17 solvents (12 esters, 4 ethers, 1 alcohol)	1	0–51	2	213
	Tetramethoxysilane	1	0	2	204
	Tetraethoxysilane	1	1	2	204
	Tetrapropoxysilane, ethanol, 2-chloroethanol, ethyl carbonate, ethyl chloroformate	1	0	2	204
	19 solvents (14 alcohols, phenol, 4 esters)	1	0–63	2	207
	35 solvents (15 esters, 8 halides, 7 alcohols, 4 silanes, *n*-decane)	1	−78 to 51	2	208
	Tetrahydrofuran, tetrahydropyran, diethyl ether, Pr_2O, Bu_2O, diethyl sulfide, ethyl nitrate, *n*-heptane, CCl_4	1	−70 to 0	1	587
	Dioxane	1	−43 to 0	1	587
	Dibenzyl ether, β,β′-dichlorodiethyl ether, *o*-nitrotoluene, diphenyl ether	1	−15 to 0	1	587
	Nitrobenzene	1	0	1	587
	Anisole	1	−61 to 0	1	587
	n-Butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl alcohols	1	25	2	271
	Ethylene glycol	To 0.424	25	1	453
		1	10	2	210
	$HO(CH_2)_3OH$, $HO(CH_2)_4OH$, $HO(CH_2)_5OH$	1	10	2	210
	n-Butane	4.4–36	20–82	1	465
	2,4,4-Trimethyl-1-pentene, 2,4,4-triethyl-2-pentene	4–10 mm	−78.5	1	77
	n-Heptane	29–71 mm	−78.5	1	77
	n-Hexane	16–82	25	1	454
	n-Decane	1	0	2	196
	Cyclohexane	20–650 mm	20–40	2	650
		100–800 mm	10–40	1	615
	Benzene	1.5–570 mm	30	1	529
		0.2–0.6	25	1	453
		6–463 mm	30–40	1	456
	Toluene	To 174 mm	−84 to −46	1	76
		3.8–6.3 mm	−78.5	2	75, 77
		25–215 mm	25	1	455
	About 0.05 mole fraction solutions in *n*-heptane of benzene, toluene, *m*-xylene, mesitylene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, *t*-butylbenzene, isopropylbenzene, ethylbenzene, trifluoromethylbenzene	15–70 mm	−78.5	1	77
	About 0.1 mole fraction solutions in toluene of benzene, *m*-xylene, *p*-xylene, mesitylene, hemimellitene, pseudocumene, chlorobenzene	2–6 mm	−78.5	1	75, 77
	About 0.1 mole fraction solutions in toluene of *n*-heptane, 1-octene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, cyclohexene, *o*-xylene, 1,3,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, tetrachloroethylene, thiophene	2–6 mm	−78.5	1	77
	Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene	30–290 mm	25	1	456
	Chlorobenzene	23–250 mm	30–40	1	456
		1–60	20–250	1	586
	$CHCl_3$, CCl_4	120–700 mm	0–25	2	263
	$CHCl_3$, CCl_4, $C_2H_4Cl_2$, $C_2H_2Cl_4$	1	20–40	0	684
	β,β-Dichloroethyl ether, anisole	10–500 mm	20–40	2	457
	Phenetole, *n*-butyl phenyl ether, diphenyl ether	To 500 mm	10–30	1	458
	Diamyl ether, diisopropyl ether, dibutyl ether, $C_2H_5OCH_2C_6H_5$, $CH_3OCH_2C_6H_5$, $C_4H_9OCH_2C_6H_5$, $(ClCH_2)_2O$, $(ClCH_2CH_2)_2O$, $(C_6H_5)_2O$, diisoamyl ether, $CH_3OC_6H_5$, $(C_6H_5CH_2)_2O$, $(ClCH_2CH_2CH_2)_2O$, $C_2H_5OC_6H_5$	1	10	2	209
	Nitrobenzene	4–400 mm	20–40	1	456
		0.4–0.7	25	1	453
	m-Nitrotoluene	14–167 mm	25	1	454
		To 500 mm	25–35	1	458
	o-Nitrotoluene	32–340 mm	25	1	454
	Thiophene, tetrahydrothiophene, phenyl sulfide, diphenyl sulfide, *n*-butyl sulfide, di-*n*-butyl sulfide, isopropyl sulfide, diisopropyl sulfide	1	0	2	196
	$AlCl_3$ in toluene	0.5–230 mm	−84 to −45	2	76
Hydrogen bromide	2-Chloroethanol	1	4–39	2	213
	2,2,2-Trichloroethanol	1	0–26	2	213
	n-Pentyl borate	1	0–34	2	213
	Ethanol		25	1	151
	n-Butane, *n*-hexane, $AlBr_3$ solutions in *n*-butane and *n*-hexane	0–2	5–25	1	192
	n-Decane	1	0	2	196
	n-Hexane, *n*-octane, *n*-decane	50–700 mm	25–45	1	59
	Benzene, toluene	80–430 mm	25	1	455

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	$CHCl_3$, CCl_4	155–665 mm	0–25	2	263
	o- and *m*-nitrotoluene	20–500 mm	25	1	455
	Thiophene, tetrahydrothiophene, phenyl sulfide, *n*-butyl sulfide, di-*n*-butyl sulfide, isopropyl sulfide, diisopropyl sulfide, diphenyl sulfide	1	0	2	196
Hydrogen iodide	Thiophene, tetrahydrothiophene, isopropyl sulfide, diisopropyl sulfide, *n*-butyl sulfide, di-*n*-butyl sulfide, phenyl sulfide, diphenyl sulfide, *n*-decane	1	0	2	196
Ammonia	Water (nomograph)				133, 137
	Methanol, ethanol		0–30	0	240
	Ethanol	7.5–10.4 mm	25–35	1	27
	n-Propyl and isopropyl alcohols		0–35	0	241
	Human blood plasma	1 mm	1–42	1	275
Phosphine	Water	118–650 mm	27–50	1	639
	Water solutions of NaCl, NaOH, and H_2SO_4	325 mm	24.5	1	639
	Xylene isomers	1	−15 to 20	0	311
	Phenyl chloride	1	0	0	311
	Benzene, toluene, C_2HCl_3, $C_2H_2Cl_4$, kerosene	1	20	0	311
Arsine	Water	200	0–26	1	286
		1	7–21	1	113
	Blood, blood serums	200 mm	21	1	286
	Aqueous solutions of NaCl, Na_2SO_4, NaOH, H_2SO_4, glycol	200 mm	20	1	286
	Monoethanolamine, triethanolamine	1	12	1	113
	HCN, methyl nitrile, ethyl nitrile, *n*-propyl nitrile	1	14	1	113
	Tetralin, acetone, CH_2Cl_2, $CHCl_3$, CCl_4, C_2HCl_3, $C_2H_4Cl_2$, $C_2H_2Cl_4$	1	25	1	113
Hydrazoic acid, HN_3	Water	2–229 mm	0–50	2	150
Nitric oxide, NO	Methyl alcohol	1	0–30	2	498
	Cyclohexane	100–800 mm	10–40	1	615
	Aqueous solutions of $CuSO_4$, $CuCl_2$, $MnSO_4$, H_3PO_4, $CoSO_4$, $NiSO_4$, $Cu_2(NH_3)_nCl_2$, Na_2SO_4 + NaOH, $FeSO_4$, $FeCl_2$	1	20	0	480
	Aqueous solutions of $FeSO_4$, $FeCl_2$	1	10–90	0	480
	Aqueous solutions of $FeSO_4$			0	199
	Nitrose liquid		40–95	0	612
Nitrous oxide, N_2O	Water	1	36	2	278
	n-Heptane, 2,2,4-trimethylpentane, benzene, CCl_4, CS_2	1	0–40	2	669
	Blood	1	36–37	2	278
		1	37	2	241A
			37.5	0	122
	Aqueous solutions of bovine serum albumin, bovine hemoglobin, bovine γ-globulin, bovine β-globulin	1	37	1	434
	Aqueous solutions of egg albumin, gelatin, serum, serum albumin, hydrated Fe and Al oxides	1	10–40	0	567
	Various homogenized tissues	1	37	2	17
		1	37	1	89
	Aqueous solutions of KCl, KNO_3, NaCl, Na_2SO_4, $Mg(NO_3)_2$, $MgSO_4$	1	0–40	2	391
Nitrogen dioxide, NO_2	Water		17–20	0	64
	Nitroglycerin	100–900 mm	20–80	0	590
Nitrosyl chloride, NOCl	Cyclohexane	100–800 mm	10–40	1	615
Sulfur hexafluoride, SF_6	Water	1	11–30	1	430
		1	0–25	1	197
	Isooctane	1	10–30	2	322
	n-Heptane, cyclohexane, methylcyclohexane, benzene, toluene, CCl_2FCClF_2, $SiCl_4$, CCl_4	1	6–33	2	15
	n-Heptane, isooctane, benzene, CCl_2FCCl_2F, $C_6H_{11}C_2F_5$, CCl_4, CS_2	1	25	2	254
	n-Perfluoroheptane	1	4–30	2	322
	Carbon disulfide	1	15–31	2	322
	Nitromethane	1	0–25	1	197
	Polyethylene, hydropol, and natural rubber	1	25	1	414
	Homogenized lung tissue	1	37	1	89
	Water saturated with nitromethane	1	25	1	197
	Aqueous solutions of NaCl, LiCl, HCl, KCl, NH_4Cl, $BaCl_2$, Na_2SO_4, KI, KBr, KNO_3, NMe_4I, NEt_4Br	1	25	1	430
Sulfur dioxide, SO_2	Water	50–1445 mm	25–115	2	44
		To 0.0038	10–32	1	467
	Water (nomograph)				129, 130, 134, 135

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
	Ethanol	4.7–6.8 mm	25–35	1	27
	1-Heptanol	2–20	25–93	1	8
	Methyl acetate		25	1	238
	Ethyl laurate	1.4–19	25–93	1	8
	Benzene	1.2–2.7	26	2	273
	Solar, spindle, and green oil		30–100	0	19
	Acetone		25	1	238
	Tetraethylene glycol dimethyl ether, N,N-dimethylacetamide, N,N-dimethylformamide, 2-octanone, nitrobenzene	1.4–19	25–93	1	8
	Dimethyl sulfoxide			0	574
	Titanium tetrachloride	1	0–100	1	676
	Aqueous solutions:				
	$ZnSO_4$	1	20–100	1	276
	$NaHSO_3$	1	20–90	2	348
	$NaHSO_3$			0	193
	NH_3	0–800 mm	15–30	2	148
	NH_3	100–750 mm	4.5–25	1	394
	$Ca(HSO_3)_2$	70–760 mm	10–25	0	644
	$Mg(HSO_3)_2$	729 mm	35	1	102
	H_2SO_4	To 0.0038	10–32	1	467
	Oleum	1	20–60	1	419
Osmium tetroxide, OsO_4	Nitromethane	1	25	1	197
Uranium hexafluoride, UF_6	Heavy oils	0–0.16	93	1	357
Methylsilane	Methyl trichlorosilane	1–25	−20 to 50	1	552
Organic Vapors					
Methanol	12 solvents, including amines, amides, nitriles, and glycols	Vap press at 4.5°	32	2	111
Ethanol	Triethylenetetramine, methylated triethylenetetramine, hexamethylenediamine, N,N-dimethylacetamide, ethylene glycol, triethyl phosphate	Vap press at 4.5°	32	2	111
n-Propyl alcohol	Triethylenetetramine, hexamethylenediamine	Vap press at 4.5°	32	2	111
Isopropyl alcohol	Triethylenetetramine, hexamethylenediamine	Vap press at 4.5°	32	2	111
n-Butyl alcohol	Triethylenetetramine, hexamethylenediamine	Vap press at 4.5°	32	2	111
sec-Butyl alcohol	Triethylenetetramine, hexamethylenediamine	Vap press at 4.5°	32	2	111
t-Butyl alcohol	Triethylenetetramine, hexamethylenediamine	Vap press at 4.5°	32	2	111
Benzene	Ethanol, acetone	<2 mm	25–35	2	27
	Aq 1 *N* KCl, KI, NMe_4I, NEt_4Br		25	1	430
Phenyl chloride	Ethanol, acetone	<1 mm	25–35	2	27
Carbon tetrachloride	Ethanol	1.0–1.7 mm	25–35	1	27
Acetone	Water	2–240 mm	15–45	1	464
	Ink and lube oils	10–140 mm	15–35	1	464
Nitromethane	Olive oil	3–12 mm	20	0	383
Methylamine	Water, ethylene glycol, glycerol, diethylene glycol	Vap press at 4.5°	32	2	111
Diethylamine	Ethylene glycol, glycerol	Vap press at 4.5°	32	2	111
n-Propylamine	*n*-Octyl alcohol, ethylene glycol, 1,3-butylene glycol, glycerol, diethylene glycol, triethylene glycol	106 mm	32	2	111
Isopropylamine	Ethylene glycol, diethylene glycol, triethylene glycol	223 mm	32	2	111
n-Butylamine	Ethylene glycol, di-, tri-, and tetraethylene glycol, hexamethylenediamine, triethylenetetramine	24 mm	32	2	111
Isobutylamine	Ethylene glycol	45 mm	32	2	111
sec-Butylamine	Ethylene glycol	57 mm	32	2	111
Mixtures of Gases					
He + CH_4	Water	200–600	25	0	441
Ar + N_2	Sea water	1	0–27	2	41
Ar + N_2	Liq NH_3	25–100	0–25	0	118
Ar + N_2	Liq NH_3	50–75		1	116
Ar + CH_4	Water	291–485	25	0	443
Ar + CH_4	Liq NH_3			0	112
H_2 + O_2	Water	36–82	149	0	583
H_2 + N_2	Liq NH_3	150–800	−10 to 50	0	63

TABLE V (*Continued*)

Gases	Solvent	Pressure, atm	Temp, °C	Measurement value (see section VI)	Ref
$H_2 + N_2$	Liq NH_3	100–500	−50 to 50	0	361
$H_2 + CO$	Hydrocarbons			0	9
$H_2 + CO_2$	Water	25–300	25	0	679
$H_2 + CO_2$	Methanol	To 60	−45	0	561
$H_2 + N_2 + CO$	Diesel fuels	3–40	25–50	1	368
$H_2 + O_2 + CO$	Diesel fuels	3–40	25–50	1	368
N_2, O_2, CO_2, C_3H_8, C_5H_{10}	Paraffin oil			0	377
$N_2 + CO_2$	Water	25–300	25	0	679
$N_2 + CO_2$	Water and aq K_2SO_4, K_2CO_3, KOH, K_2CO_3–$KHCO_3$			0	214
$N_2 + CO_2$	Crude oils	0–300	50	0	519
$N_2 + CH_4$	Diesel fuels	3–40	25–50	1	368
$N_2 + CH_4$	Aq NaCl and $CaCl_2$	50	4–45	0	376
$N_2 + CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$	Aq $CaCl_2$ and NaCl	1–3	4–45	0	376
$N_2 + CO_2 + C_3H_8$	Crude oils	0–300	100	0	519
$CO_2 + H_2S$	Water		20	0	226
$CO_2 + H_2S$	Monethanolamine in water	1–3000 mm	40–140	2	283
$CO_2 + CS_2$, $CO_2 + COS$	Over piperidine or morpholene-satd kerosene			1	236
$CO_2 + CH_4$, $CO_2 + C_2H_4$, $CO_2 + CH_4 + C_3H_8$, $CO_2 + C_2H_4 + C_3H_8$	Crude oil	0–300	50	0	519
$N_2O + O_2$, N_2O + ether	Blood	1	37	1	241A
$CH_4 + C_4H_{10}$, $CH_4 + C_2H_6$	Crude oil	High press		0	607
$C_3H_8 + C_4H_8$	Paraffin oil	180–700 mm	20	1	377
Natural gas	Crude oil	200		0	627
Natural gas	Water	1	0–70	0	438

TABLE VI
SOLUBILITY DATA FOR GASES IN MOLTEN SALTS AND GLASSES

Gases	Solvent	Pressure	Temp, °C	Measurement value (see section VI)	Ref
Helium	3 Na-Ca glasses and 7 alkali glasses	1 atm	1200–1480	1	435
	Binary and ternary glass melts		1200–1480	0	546
	2 lithium silicate glasses	1 atm	1400	1	545
	Pyrex glass		25–515	0	506
	Sodium disilicate	10 mm	800	1	444
	Pyrex 774	10 mm	1170	1	444
	KCl	646–698 mm	900, 1300	0	201
	Gabbrodiabase	513, 716 mm	1300	0	201
	LiF–BeF_2 (64:36 mole %)	1–2 atm	500–800	1	635
	NaF–ZrF_4 (53:47 mole %)	0.4–2 atm	600–800	1	232
	NaF–ZrF_4–UF_4 (50:46:4 mole %)	0.2–2 atm	600–800	1	232
	LiF–NaF–KF (46.5:11.5:42.0 mole %)	1–2 atm	600–800	1	50
Neon	LiF–BeF_2 (64:36 mole %)	1–2 atm	500–800	1	635
	NaF–ZrF_4 (53:47 mole %)	1–2 atm	600–800	1	232
	LiF–NaF–KF (46.5:11.5:42.0 mole %)	1–2 atm	600–800	1	50
Argon	Sodium disilicate	10 mm	800	1	444
	Pyrex 774	10 mm	1170	1	444
	LiF–BeF_2 (64:36 mole %)	1–2 atm	500–800	1	635
	NaF–ZrF_4 (53:47 mole %)	0.5–2 atm	600–800	1	232
	LiF–NaF–KF (46.5:11.5:42.0 mole %)	1–2 atm	600–800	1	50
Xenon	LiF–BeF_2 (64:36 mole %)	1–2 atm	600–800	1	635
	NaF–ZrF_4 (53:47 mole %), NaF–ZrF_4–UF_4 (50:46:4 mole %)	1–2 atm	600–800	1	232
Hydrogen	Molten slag		1400–1800	0	451
	Sodium disilicate	10 mm	800	1	444
	Pyrex 774	10 mm	1170	1	444
	NaOH, KOH	100–800 psia	410–500	2	589
Nitrogen	$NaNO_3$, KNO_3, $CsNO_3$	1 atm	300–400	0	195
Oxygen	Sodium disilicate	10 mm	800	1	444
	Pyrex 774	10 mm	1170	1	444
	$NaNO_3$, KNO_3, $CsNO_3$	1 atm	300–400	0	195
Chlorine	NaCl, KCl, $MgCl_2$	1 atm	800–1050	1	511
	1:1 KCl–NaCl, NaCl–$MgCl_2$, KCl–$MgCl_2$	1 atm	565–1050	1	511
Carbon dioxide	Glass	1 atm	1100–1315	1	385
	NaCl, KCl	1 atm	810–950	1	233, 346

TABLE VI (*Continued*)

Gases	Solvent	Pressure	Temp, °C	Measurement value (see section VI)	Ref
Hydrogen fluoride	$NaF-ZrF_4$ (53:47, 45:55, 80.5:19.5 mole %)	0.5–3 atm	550–800	1	553
Water vapor	Binary and ternary glasses		1250–1750	0	546
	Sodium silicate	0.06–1 atm	900–1100	1	602
	LiCl–KCl (50:50, 53:47, 60:40, 69:31 mole %)	3–26 mm	390–480	1	82, 83
	Alkali nitrates and perchlorates	To 60 mm	145–290	1	154
	$NaNO_3$, KNO_3, $CsNO_3$	16–21 mm	300–400	1	195
	$CsNO_3-Ba(NO_3)_2$ (95.7:4.3 mole %)	16–21 mm	391	1	195
	$KNO_3-Ba(NO_3)_2$ (99:1, 96:4 mole %)		332	1	195
	$KNO_3-K_2Cr_2O_7$ (98:2 mole %)		329	1	195
	$NaNO_3-Ca(NO_3)_2$ (96:4 mole %)		299	1	195
Sulfur trioxide	Glass		900	0	45
Boron trifluoride	$LiF-BeF_2-ZrF_4-ThF_4-UF_4$ (65:28:5:1:1 mole %)	1.2–1.9 atm	500–700	1	554

TABLE VII

SOLUBILITY DATA FOR GASES IN MOLTEN METALS AND ALLOYS (ARRANGED BY INCREASING ATOMIC NUMBER OF THE METAL)

Metal	Gas	Pressure	Temp, °C	Ref
Lithium	Nitrogen		250–300	257
			250–400	256
	Oxygen		121–204	257
			250–400	256
Sodium	Oxygen		130–540	448
Magnesium	Hydrogen		550–775	326
			760	528
Aluminum	Hydrogen	1 atm	660–1050	158
		1 atm	700–1000	33
		1 atm	670–850	489
		50–800 mm	700–1000	462
		200–600 mm	700–900	258
Silicon	Oxygen		1410	1
Chromium	Hydrogen	1 atm	1903	636
	Nitrogen	1 atm	1600, 1700	638
		1 atm	1600–1750	432
			...	433
Manganese	Nitrogen	1 atm	1300–1450	26
		1 atm	1273–1500	225
		1 atm	1600, 1700	638
Iron	Hydrogen	1 atm	1680–2460	354
		1 atm	1536–1820	636
				664
		1 atm	1580–1670	537
			1560, 1655	665
		1 atm	1600	86
			Mp to bp	355
		1 atm	1592	637
		1 atm	1556–1744	370
		10–40 mm	1560, 1685	296
		20–40 mm	1275–1420	356
	Nitrogen	1 atm	1550–1700	535
		1 atm	1600	86
		1 atm	1600	298
		To 4 atm	1560	538
		10–30 mm	1550–1750	295
		1 atm	1550–1700	159
			Mp and up	242
		1 atm	1600	598
			1530–1750	521
	Oxygen	Satd FeO slag	1510–1760	536
			1530–1700	186
		1 atm	1550–1700	595
		Satd FeO	1535–1670	598
		Satd FeO	1550–1650	245
		Satd SiO_2 or MnO	1550–1650	246
		Satd FeO	1530–1700	184
		H_2-H_2O equil		372
		H_2-H_2O equil	1600, 1650	380
		Satd SiO_2	1525–1725	534
Cobalt	Hydrogen	1 atm	1592–1758	636
	Oxygen	1 atm	1490–1700	595
Nickel	Hydrogen	1 atm	1523–1709	636
		1 atm	1500–1600	537
		1 atm	1600	86
	Nitrogen	1 atm	1600, 1700	638

TABLE VII (*Continued*)

Metal	Gas	Pressure	Temp, °C	Ref
	Oxygen	1 atm	1450–1690	65
			1470–1720	182
		1 atm	1465–1700	595
		Satd NiO	1450–1691	663
		CO_2–CO equil	1726–1970° K	65
				524
Copper	Hydrogen	1 atm	945–1100	636
			Mp–1400	306
		5–760 mm	1100–1300	43
	Sulfur dioxide	100–760 mm	1150, 1240	279
		1–760 mm	1100–1300	190
				189
Zinc	Hydrogen			306
				258
	Nitrogen		448	258
Silver	Krypton			281
Cadmium	Krypton	1 atm	1100–1150	280
	Hydrogen			306
Indium	Krypton	1 atm	1000–1300	280
Tin	Krypton		1100–1300	281
	Hydrogen	1 atm	1000–1300	43
Mercury	Helium	High press	20–140	431
	Hydrogen		Mp and up	306
Lead	Krypton		800–1300	281
	Hydrogen		516	258
	Oxygen	Satd $PbO–SiO_2$	1000	126
		Air atm	400–900	525
		Satd $PbO–SiO_2$	1000–1194	500
		Air atm	350–800	30
Bismuth	Xenon		540	171
Alloys				
Fe + V, Fe + B	H_2		1560, 1655	665
Fe + Ni	H_2	1 atm	1400, 1600	304
Fe + Cr	H_2	1 atm	1400, 1600	304
Fe + Ni	H_2	1 atm	1600	86
Ni + Co	H_2	1 atm	1600	86
Fe + Co	H_2	1 atm	1600	86
Steel	H_2		1600	658
Fe alloys with Al, B, C, Co, Cu, Ge, P	H_2	1 atm	1592	637
Cu–Zn	H_2			306
Al–Cr, Al–Fe, Al–Th, Al–Ti, Al–Sn	H_2	1 atm		33
Cu–Sn	H_2	5–760 mm	1100–1300	43
Fe–Si	H_2	1 atm		370
Fe–Ti, Fe–Nb, Fe-Ta	H_2	10–40 mm	1560, 1685	296
Mg–Al, Mg–Zn	H_2		760	528
Al–Cu, Al-Si	H_2		700–1000	462
Fe with C, Mn and Si	H_2	20–40 mm	1275–1420	356
Fe–V	N_2	1 atm	1580	331
Mn–Fe, Mn–Si	N_2	1 atm	1410–1660	25
Fe alloys with Cr, Co, Nb, Cu, Mn, Mo, Ni, Si, Ta, Sn, W, and V	N_2	1 atm	1600	472
Fe–Mn	N_2	1 atm	1245–1550	34
Fe alloys with Co, Cu, Ni, C, Mo, Si, S, and Se	N_2	1 atm	1550–1650	535
Fe–Ni, Fe–Co	N_2	1 atm	1600	86
Fe–Mo–V	N_2	1 atm	1600–1900	298
Fe–Ni, Fe–Mo, Fe–V	N_2	1 atm	1600–1800	298
Fe–V	N_2		1580–1650	332
Fe containing P and O	N_2	75–570 mm	1600	185
Fe–Mn, Fe–Si, Fe–Mo	N_2	To 4 atm	1560	538
Steel	N_2	Variable	1600	658
Fe–Si	N_2	10–30 mm	1550–1750	295
Fe–C, Fe–Al	N_2	1 atm	1550	159
Fe–Cr, Fe–V	N_2	1 atm		73
Welding alloys	N_2		1550–1600	48
Mn–Fe, Mn–Cr, Ni–Cr	N_2	1 atm	1600, 1700	638
Fe with small amounts of C, Si, Mn, Cr, Ni	N_2		1530–1750	521
Fe–Mn, Fe–Cr, Fe–Ni (entire range of compn)	N_2		1530–1750	521
Fe–Cr, Fe–Mn, Fe–Ni	N_2		1600	521
Cr–Si	N_2	1 atm	1600–1750	432
Cr–Si	N_2			433
Fe–Cr	N_2	512, 735 mm	1550, 1670	350
Fe containing S	O_2		1550, 1600	523
Na–K	O_2		20–176	448
Fe–S	O_2		1550–1600	87
Fe–Ni	O_2		1470–1720	182
Fe–Si	O_2	1 atm	1600	264
Fe–Cr	O_2	Atm press	1650–1750	125
Steel	O_2	Variable press	1600	658
Fe–Al	O_2	Satd FeO	1550–1650	245
Fe–Si, Fe–Mn, Fe–Si–Mn	O_2	Satd SiO_2 or MnO	1550–1650	246
Fe–Cr, Fe–Ni	O_2	H_2–H_2O equil	1625	371

TABLE VII (*Continued*)

Alloy	Gas	Pressure	Temp, °C	Ref
Fe-Cr, Fe-Ni	O_2	H_2-H_2O equil		372
Fe-Cr, Fe-Cr-Ni	O_2	H_2-H_2O equil		47
Ni-Fe	O_2	Air atm or satd NiO	1450-1691	663
Fe-Cr-P, Fe-Ni-P	O_2	H_2-H_2O equil	1500-1650	365
Fe-Ti	O_2	H_2-H_2O equil	1600, 1650	380
Fe-P	O_2	H_2-H_2O equil	1500-1650	366
Fe-Ni	O_2			524
Cu-Ni	O_2	H_2-H_2O equil	1380-1620	596

TABLE VIII
PARTIAL MOLAL VOLUMES OF GASES IN LIQUIDS

Gases	Solvent	Temp, °C	Pressure, atm	Ref
Helium	Water (hydrostatic pressure)	25	1-102	169
	Liquid methane	−183, −167	To 160	229
Argon	Water (hydrostatic pressure)	1-25	1-102	169
	Isooctane, methylcyclohexane, toluene, perfluoromethylcyclohexane, carbon tetrachloride, bromoform, carbon disulfide	25	1	282
	n-Hexane, *n*-octane, methanol	30	100	397
Hydrogen	Water	25-100		324
	Water, methanol	0-50	1	336
	Methyl acetate, benzene, acetone, ethyl ether, chlorobenzene, CCl_4	25	1	261
	Liquid methane	−183 to −146	180-220	177
	Methane, ethane, ethylene, propane, butane	−183 to −4	High press	37
	n-Heptane, *n*-octane	25-50	50-300	352
	n-Octane, benzene	130-260	To 150	101
	Cyclohexane	20-60	700	337
	Benzene, toluene, *n*-perfluoroheptane	25	1	282, 633
	Benzene	25	27-775	340
	Liquid argon	−186 to −133		630
Deuterium	*n*-Heptane, *n*-octane	25 to 50	50-300	352
	Benzene, toluene, *n*-perfluoroheptane	25	1	282, 633
	Liquid argon	−186 to −153		630
Nitrogen	Water	0	1	359
	Water (hydrostatic pressure)	25	1-102	169
	Water, methanol	0-50	1	336
	Methyl acetate, benzene, acetone, ethyl ether, chlorobenzene, CCl_4	0, 25	1	261
	n-Hexane	30	100	397
	Benzene	25	27-775	340
	n-Perfluoroheptane	25	1	220
Oxygen	Water	0	1	359
	Water	25	1-102	169
	Water, methanol	0-50	1	336
	Methyl acetate, benzene, acetone, ethyl ether, chlorobenzene, CCl_4	0, 25	1	261
Air	Water, methanol	25	1	336
Chlorine	*n*-Heptane	0, 25	1	219
Methane	Water	38-170		324
	Water	17-36	1	396
	Water, methanol	0-50	1	336
	Methyl acetate, benzene, acetone, ethyl ether, chlorobenzene, CCl_4	0, 25	1	261
	n-Hexane, *n*-heptane, isooctane	27	1	548
	n-Hexane, *n*-perfluoroheptane, carbon disulfide	25	1	220
Ethane	Water	38-170		324
	Water	17-30	1	396
	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	10-40	1	261
	n-Hexane, *n*-perfluoroheptane, carbon disulfide	0-25	1	220
Propane	Water	38-170		324
	Water	17-30	1	396
Ethylene	Water, benzene, methanol, tetrahydrofuran	25-150	To 193	253
	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	10-40	1	261

TABLE VIII (*Continued*)

Gases	Solvent	Temp, °C	Pressure, atm	Ref
Acetylene	Water, benzene, methanol, acetone	10–40	29	316
	Water, benzene, methanol, tetrahydrofuran	20–45	To 39	253
	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	10–40	1	261
	21 solvents	−20 to +20	3.5–14	516
Dimethyl ether	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	25	1	261
Methyl chloride	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4, chloroform	25	1	261
Carbon monoxide	Water, methanol	0–50	1	336
	Methyl acetate, benzene, acetone, ethyl ether, chlorobenzene, CCl_4	0, 25	1	261
Carbon dioxide	Water	0	1	359
	Water (hydrostatic pressure)	25	1–102	169
	Water, methanol	0–50	1	336
	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	25	1	261
Nitrous oxide	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	25	1	261
Sulfur dioxide	Methyl acetate, benzene, acetone, chlorobenzene, CCl_4	10–40	1	261
Sulfur hexafluoride	*n*-Heptane, isooctane, benzene, CCl_4, CCl_2FCCl_2F, $C_6H_{11}C_2F_5$, CS_2	25	1	254
Carbon tetrafluoride	*n*-Heptane, isooctane, benzene, CCl_4	27	1	548

of the experimental values for all the metals except lead for which H was 12 kcal/mole too large. The calculated vibrational entropies agreed within experimental error.

VI. SOLUBILITY DATA

This section concerns four tables. Table V is arranged according to gas, giving the solvent employed, the temperature and pressure range of the measurements, and a reference. In addition, a critical value was assigned to each measurement: 2—the data are quantitative and the precision is probably better than 2%; 1—the data are quantitative but the precision is poorer than 2%; 0—the data are either just qualitative or it was not possible to determine the level of precision of the measurements. These values were arrived at by using the author's own statements and/or our critical evaluation of the method employed. Where there are blanks under the headings of temperature and pressure, it was not possible to determine these ranges. For each gas the solvents were systematically and consistently arranged. Reference to nomographs are listed under the gas in this table. Obviously no nomograph can be better than the experimental data on which it is based. Before using a nomograph the literature should be examined to determine whether or not the nomograph has been superseded by more reliable data.

Table VI gives references to the solubility of gases in molten salts and glasses and is arranged by gas.

Table VII gives references to the solubility of gases in molten metals, and alloys. This table is arranged according to increasing atomic weight of the metal with the alloys at the end. No value judgments were made on these solubilities.

Table VIII gives references to the partial molal volume determinations of gases in liquids. This information is arranged by gas and is included since it is not only interesting in its own right but is valuable for the use and evaluation of theories of gas solubility.

ACKNOWLEDGMENT.—This investigation was supported in part by a PHS Grant No. GM12071 from the National Institutes of Health, Public Health Service. The authors take pleasure in acknowledging the early interest, encouragement, and advice of Professors P. M. Gross and J. H. Saylor.

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Journal of Chromatography, 158 (1978) 277–293
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CHROM. 11,148

THE ROLE OF DISSOLVED GASES IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Dissolved gases are usually present as components of the mobile phase in high-performance liquid chromatography. Each gas has its unique properties and affects the chromatographic system in different ways.

The solubility in pure and mixed solvents is explored experimentally and compared with data already in the literature. It is found that the non-linear solubility characteristics in binary solvent systems account for the observed evolution of large quantities of gas when air-saturated solvents are mixed in chromatographs. The degassing requirements in one-pump, low-pressure-mixing gradient architectures are compared with those of conventional two-pump, high-pressure-mixing systems.

Dissolved oxygen affects detector performance in several ways. It forms a UV light-absorbing complex with many solvents. Changes in oxygen concentration therefore cause UV detector drift. The magnitude of this effect varies markedly with different solvents, and is particularly pronounced at wavelengths below 260 nm. Dissolved oxygen quenches fluorescence of both solvents and solutes. As a consequence, fluorescence detector drift and responsivity depend on oxygen concentrations. Maximum fluorescence sensitivity can only be achieved with deoxygenated mobile phases.

Because of these facts, analytical precision requires that gas concentrations be carefully controlled. The various control techniques are discussed: heating, boiling, vacuum, ultrasonics and gas sparging. A new method of helium degassing is described which eliminates bubble formation and maintains the level of all other gases at zero concentration.

INTRODUCTION

Because air is ubiquitous, the gases which comprise it tend to be found in high-performance liquid chromatography (HPLC) mobile phases. Their presence accounts for a variety of effects, many of which interfere with sensitive, precise, trouble-free chromatographic analysis. Although some of these problems have been understood for some time, others have received scant attention. There is little overall awareness of the important role of gases, and that which does exist is often based on misunderstanding.

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The importance of excluding dissolved oxygen from the mobile phase in order to protect labile stationary phases has been mentioned in most standard texts on HPLC[1–3]. Leitch documented the improved column lifetime and analytical precision resulting from deoxygenated solvents[4]. Exposure of the liquid–liquid partition column (3,3′-oxydipropionitrile) to dissolved oxygen during constant or heavy use severely reduced column life.

The potential for harm to the mobile phase has also been pointed out[2]. Butyl ether mobile phase was oxidized during handling and storage in the reservoir, forming peroxides which reacted with the stationary phase and changed its polarity. The susceptibility of other ethers, such as tetrahydrofuran, may also be a problem[5].

Snyder[6] has counciled about the benefits of excluding oxygen in liquid–solid (adsorption) chromatography, since sample oxidation is often increased by the presence of the adsorbent. A recent example[7] in reversed-phase chromatography described the ease with which aniline and its metabolites were oxidized during chromatography, and the improved results with deoxygenated mobile phases compared to mobile phases to which antioxidants had been added.

The improvement of detector performance resulting from deoxygenating the mobile phase has also been reported. Fox and Staley[8] showed that deoxygenated mobile phases in polycyclic aromatic hydrocarbon analysis produced a limit of detection for benzo[*a*]pyrene which was nearly four times as sensitive than when air-saturated mobile phase was used. Different but linear calibration curves were obtained in the presence and absence of dissolved oxygen. Compared to pyrene, oxygen quenching of fluorescence is less important in chrysene but more important in benzo- and dibenzopyrenes. They did not determine how effective or reproducible their deoxygenation process was. Chamberlain and Marlow[9] demonstrated that oxygen dissolved in the mobile phase caused increased noise levels and decreased standing current in the LC electron capture detector they used.

Perhaps a more generally encountered problem than any of the above is the occurrence of gas bubbles in the detector[1–3]. Air dissolved in the carrier at high pressure can subsequently form bubbles in the mobile phase as it passes through the detector, causing noise and drift. Gas bubbles also affect pump performance, but this has not been a serious concern prior to the advent of one-pump, low-pressure-mixing chromatograph architectures[10–13].

Some of the above reports contain misunderstandings about the solubility behavior of air gases. For example, it has been said that the more polar the mobile phase, the greater the tendency to dissolve air[1,9]. Actually the opposite is true. Water is the least hospitable solvent for gases. And the bubble problems are attributed to oxygen[1,4,14], whereas nitrogen is as much a source of difficulty.

The purpose of this paper is to report new findings on gas behavior of chromatographic significance, and to describe ways of improving the reliability, sensitivity and analytical precision of HPLC by careful control of dissolved gases. We will proceed by (1) reviewing gas solubility behavior in pure solvents and binary mixtures, (2) comparing the one-pump, low-pressure-mixing gradient architecture with the two-pump, high-pressure mixing gradient architecture, as to gas solubility problems, (3) describing methods of controlling dissolved gas concentrations, (4) discussing the "optical properties" of dissolved gases so as to explain observed UV and fluorescence detector artifacts, including UV detector behavior which has not been reported before in the chromatographic literature and (5) commenting on other aspects of dissolved gases, including the effect of carbon dioxide on mobile phase pH and therefore on the reproducibility of retention times and peak areas.

EXPERIMENTAL

Column, solvents and samples

Stainless-steel columns (250 × 3.1 mm I.D.) packed with 10-μm Spherisorb ODS and 250 × 4.6 mm I.D. stainless-steel columns packed with 10-μm LiChrosorb RP-8 were used. Both are totally porous, bonded reversed-phase packings which are respectively octadecyl (C_{18}) functionality on spherical silica and octyl (C_8) functionality on irregular silica. (Spectra-Physics, Santa Clara, Calif., U.S.A.)

Mobile phases were prepared from distilled-in-glass solvents (Burdick & Jackson, Muskegon, Mich., U.S.A.). Water was prepared by a Milli-Q system, fed by a Milli-RO system, in turn fed by Santa Clara (Calif., U.S.A.) tap water; the Milli-Q had four cartridges, two mixed-bed ion exchangers followed by two activated carbon units (Millipore, Bedford, Mass., U.S.A.). Solvents were degassed as indicated in the text.

Sparging gases were high purity grades, exceeding 99.99 mole% purity. Air was "breathing quality". Samples were from Chem Service (West Chester, Pa., U.S.A.) and Aldrich (Milwaukee, Wisc., U.S.A.). They were dissolved in water–methanol and water–acetonitrile mixtures.

Control of flow, composition and temperature

A Spectra-Physics Model SP 8000 research liquid chromatograph and a Spectra-Physics Model 3500B gradient liquid chromatograph were used. The former employs a single pump, attached to a low-pressure composition forming module (ternary proportioning valve). It has ±0.1 °C column temperature control via a forced air oven. The 3500B system employes a dual reciprocating piston pump for solvent A and an identical but independent one for solvent B. The composition is formed at high pressure in a dynamically stirred chamber. Temperature control was via a water bath.

The detectors were Spectra-Physics Model SP 8310 operated at 254 nm, Model SP 770 variable-wavelength detector and Model SP 970 fluorescence detector.

RESULTS AND DISCUSSION

Gas solubility in pure solvents

The solubilities of gases in liquids have long been an area of active interest to chemists. Practical concern has been related to such diverse fields as industrial processes and the composition of artificial atmospheres. Theoretical concern has been related to the small solubility and the variety of gases available to use as probes for the investigation of liquid and solution structure and properties. A number of excellent review articles exists[15–18]. There are several major sources[19–21] for gas solubility data in pure solvents in addition to these reviews. Solubility data in mixed solvents is of course of the greatest interest to the chromatographer since the use of a pure solvent mobile phase is rare except in exclusion chromatography. Unfortunately, the data for such realistic mobile phases is scanty, although a few papers exist[22–25] which describe the solubility of some air gases in aqueous alcohol solutions.

Before proceeding further it may be instructive to review briefly a few of the salient facts about gases. Air comprises 78.08% N_2, 20.95% O_2, 0.93% Ar, 0.03% CO_2 and less than 0.01% other gases. Gases in a mixture behave essentially independently, the solubility of the individual gases in a mixture of gases being directly proportional to their partial pressures (Dalton's law). Different gases have different solubilities in a given solvent. Different solvents have different solubility properties towards a given gas. The solubility of gases in liquids usually decrease with increasing temperature, but there are numerous exceptions and the correlation of solubility data as a function of temperature is not simple. Gas solubilities in most solvent mixtures, like so many physical phenomena in non-ideal solutions, are not a linear function of the composition expressed in mole fraction.

Fig. 1 shows the solubility of several gases in many solvents using data taken from refs. 17 and 18. The solubility is expressed as the mole fraction. A feel for the magnitude of these values can be gained by realizing that the carbon dioxide solubility of mole fraction 0.01 in benzene is equivalent to about 2.4 ml of carbon dioxide at 1 atm and 25°C per ml of benzene; and the nitrogen solubility of mole fraction 0.000014 in water is equivalent to about 16 μl of nitrogen at 1 atm and 25°C per ml of water. The solubility of the various gases in the various solvents thus ranges over a factor of 1000. The solubility is plotted against solvent polarity, expressed as Snyder's polarity index, P'[26]. This solvent characterization parameter is but one of several which have been proposed recently. It can be compared with the Hildebrand solubility parameter δ[27,28] in that values of P' roughly parallel values of δ, and have similar significance. However, whereas δ is measured for the pure solvent, and only reflects interactions that exist in the pure solvent, P' is measured against a variety

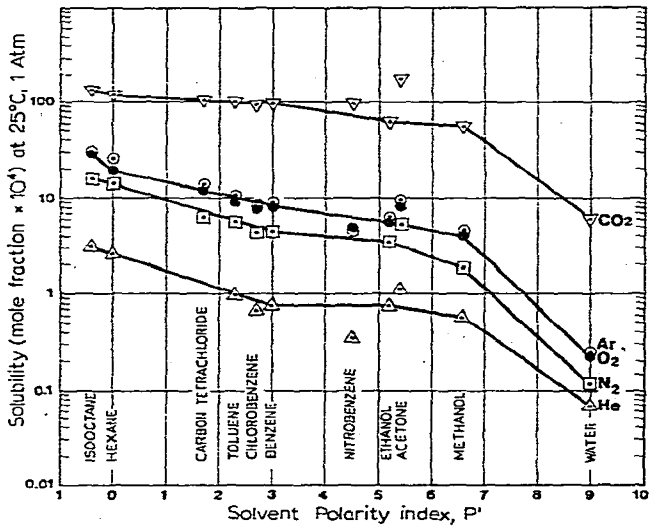


Fig. 1. Gas solubility *vs.* solvent polarity index. The solubility is expressed as mole fraction × 10^4 for pure gases in equilibrium with the solvent at 1 atm and 25 °C. The polarity index is the Snyder parameter. ∇, CO_2; ⊙, Ar; ●, O_2; ⊡, N_2; △, He.

of solutes that encompass all possible types of interaction. The Snyder parameter therefore may not be the most reasonable one to use if a smooth curve is desired, but it is employed here since it is currently popular in chromatographic literature[12]. The important point to note is that gases, being non-polar, behave as one would expect, having increasing solubility as the solvent polarity decreases.

It should be pointed out that these solubility values represent the amount of gas which will be found dissolved in the solvent at equilibrium with one atmosphere of the pure gas over the solvent. So the previously mentioned 2.4 ml of carbon dioxide in benzene only exists in a pure carbon dioxide atmosphere. Much less is in the solvent exposed to air. Hydrogen is not plotted. It falls midway between the helium and nitrogen curves, except in water, where it is slightly more soluble than nitrogen. The solubility of the rare gases increases with increasing atomic weight. In water the mole fractions for He, Ne, Ar, Kr, Xe and Rn are 0.07, 0.08, 0.25, 0.45, 0.78 and 1.68, respectively.

It is clear that water dissolves the least amount of air gases. The common misconception that it is the best solvent may derive from the fact that gas is often seen to come out of solution in water. But this may be because, once degassed, it does not take much gas to redissolve before saturation is reached. The real problem with regard to gas solubility in HPLC, however, comes with mixed solvents, either in isocratic mode where two solvents are mixed by the instrument, or in gradient mode.

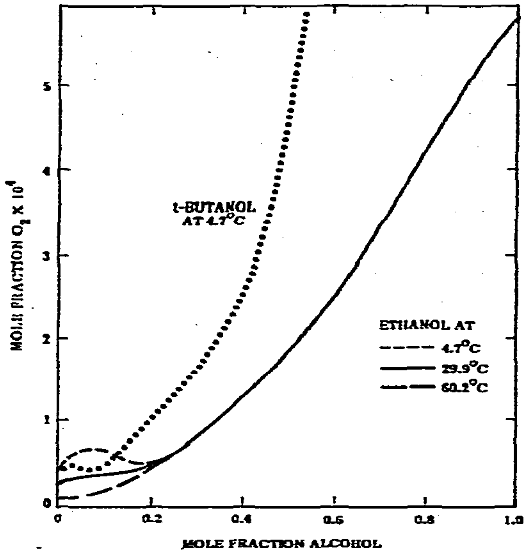
Gas solubility in mixed solvents

As previously mentioned, there is not much data in the literature on gas solubility in mixed solvents. Most data which exists is for water–alcohol mixtures, and we can infer from it what may happen in other binary mixtures of solvents, especially those binary mixtures where the two solvents interact strongly.

Ben-Naim[22] studied the solubility of argon in water–methanol systems. A plot of solubility *vs.* mole fraction of methanol shows the solubility generally increasing with increasing methanol content as one would expect. However, it goes through a maximum and then a minimum, especially at low temperature. Cargill and Morrison[23] extended the argon study over a wider temperature range, and included water–*tert.*-butanol systems. The latter exaggerated the peculiar behavior of alcohol binary mixtures. Cargill[24] also studied oxygen and found it to behave like argon. Fig. 2 shows a few of the solubility curves from the Cargill paper[24]. In the paper the solubility was expressed by S_0, defined as the volume of gas in ml, corrected to 273 °K and 1 atm, dissolved by 1 kg of solvent, under a gas pressure of 1 atm. In Fig. 2 it is expressed as mole fraction.

Fig. 2 can be contrasted with Fig. 3, which shows the amount of gas actually present in the solution at various mole fractions, starting with the A and B solvents air saturated. The significant observation is that: when two solvents, such as water and ethanol, are at equilibrium with the atmosphere (*i.e.*, air saturated) and when they are blended to form a mixture (such as in gradient elution), supersaturated conditions exist during much of the run, which cause gas to come out of solution until the concentration is at the allowed saturation level.

Fig. 4 illustrates what happens in a real chromatographic situation. It is a record of the column inlet pressure during a gradient run of 0 to 100% methanol in water in 5 min. The pumping system is the Spectra-Physics SP 8000 liquid chro-



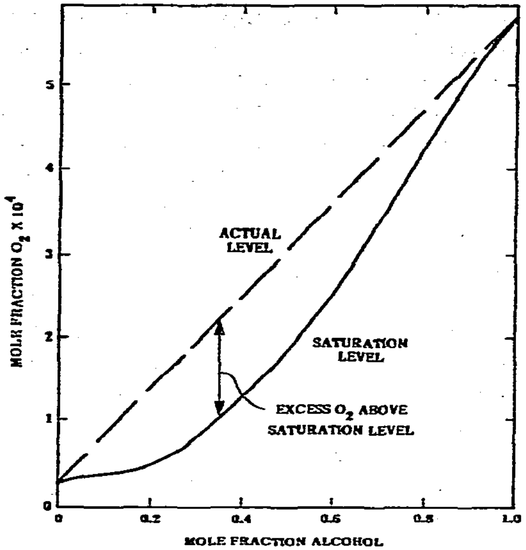


Fig. 2. Oxygen solubility in aqueous alcohol mixtures: mole fraction oxygen *vs.* mole fraction alcohol. The solubility is expressed as in Fig. 1. The original data of Cargill[24] was plotted in terms of S_0, defined as the volume of gas in ml, corrected to 0 °C and 1 atm, dissolved by 1 kg of solvent, under a gas pressure of 1 atm, on a logarithmic scale. Data reproduced by permission of the publisher.

Fig. 3. Oxygen solubility *vs.* oxygen concentration. The actual level represents the amount of oxygen in the admixtures, starting with air saturated pure water and air saturated pure ethanol. The saturation level is the allowed solubility level, the 29.9 °C curve from Fig. 2. Note the non-linear behavior, particularly at the low mole fractions of ethanol.

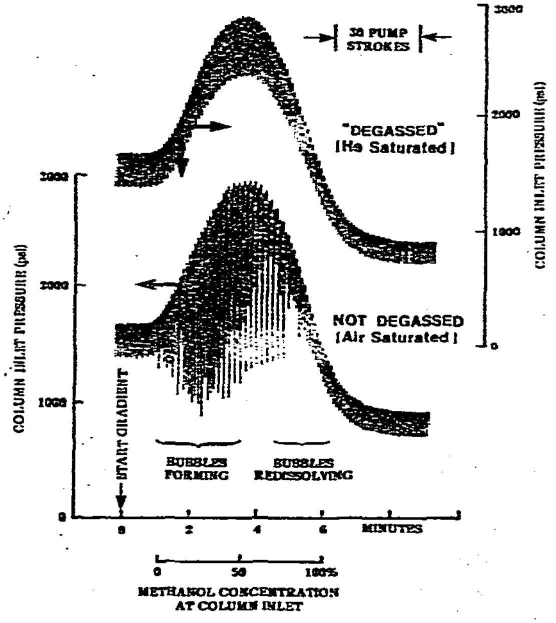


Fig. 4. Bubble formation in pump chambers with undegassed solvents. Column, 250 × 3.1 mm I.D.; packing, 10-μm Spherisorb ODS; solvent, 0–100% methanol in 5 min; flow-rate, 5.0 ml/min; pressure, as indicated; temperature, 25 °C. Recorded on the SP 8000 printer/plotter using the signal from the pre-column pressure transducer.

matograph, which has a single pump with two pump chambers each of 400-μl displacement. The flow feedback control has been turned off so that the pulsation (pressure dip) at the be ginning of each pump stroke is evident. This pulsation is a measure of the compliance in the chamber, which in turn is the sum of mechanical elasticity, fluid compressibility and the compressibility of any undissolved gas present. The upper curve exhibits the expected rise and fall of pressure during the gradient, which reflects the viscosity profile of the gradient mobile phase. The pressure pulses are uniform, demonstrating that there are no undissolved gas bubbles in the chamber. This curve was made using solvents which had been helium "degassed" (see below). The lower curve is similar, but the pressure pulses are irregular. The solvents were not degassed, but were simply equilibrated with air. These irregular pulses result from bubbles of gas entering the pump during the first part of the gradient. Later in the gradient, the pressure and solvent composition are such as to redissolve them. In some cases, especially at low operating pressures, the pulses persist because the gas never redissolves. Such behavior not only causes flow-rate errors, but is deleterious to composition precision.

The bubbles in the above example are formed in the low-pressure ternary proportioning valve, which mixes the two pure solvents in the proper proportion during the run. Fig. 5 diagrams such a system, and compares it with the conventional two-pump, high-pressure-mixing architecture. It is clear that the environment where the pure solvents are mixed is radically different in the two types. In the conventional architecture, the solvents are mixed at high pressure, where the solubility is much higher. Thus gases do not come out of solution at that point. However, if there is air in the solvents, it will come out of solution when the pressure again reaches one atmosphere, and sometimes sooner if some gas has been picked up at high pressure via a small leak in the system. For this reason, a flow restrictor is often put at the detector outlet, so that only after the detector does the pressure reach a level where gas bubbles form (see the pressure profile in Fig. 5).

Gas control methods

There are two approaches to gas control. One strives to eliminate all dissolved gases, the other to eliminate or control the concentrations of only certain gases. The former has been the most common approach directed at remedying the various problems described above, *i.e.*, gas bubbles, oxidative degradation of samples and phases, and detector artifacts. The approach used most often is vacuum degassing[1,2], the application of a vacuum to the mobile phase just prior to chromatography. Heating[2,3] and ultrasonic treatment[14,29] have also been employed. One of the gas solubility reviews[16] has a good discussion of degassing methods. It reports that the most common method to degas a solvent in non-chromatographic work is to boil away a portion of it under vacuum, a batch binary distillation. The Ramsey–Rayleigh equation for this type of distillation predicts that the evaporation of as little as 0.1% of the solvent should reduce the gas content by several 1000-fold. But the assumption of equilibrium is incorrect. In practice 10–20% of the solvent is evaporated. Other methods include pumping on the frozen solvent or boiling followed by spraying into an evacuated flask.

Sparging with a pure gas (bubbling it through the solvent) has most frequently been employed for the elimination of only certain gases[1,2]. This technique, also referred to as purging or stripping, has been used in gas chromatographic studies[16,30].

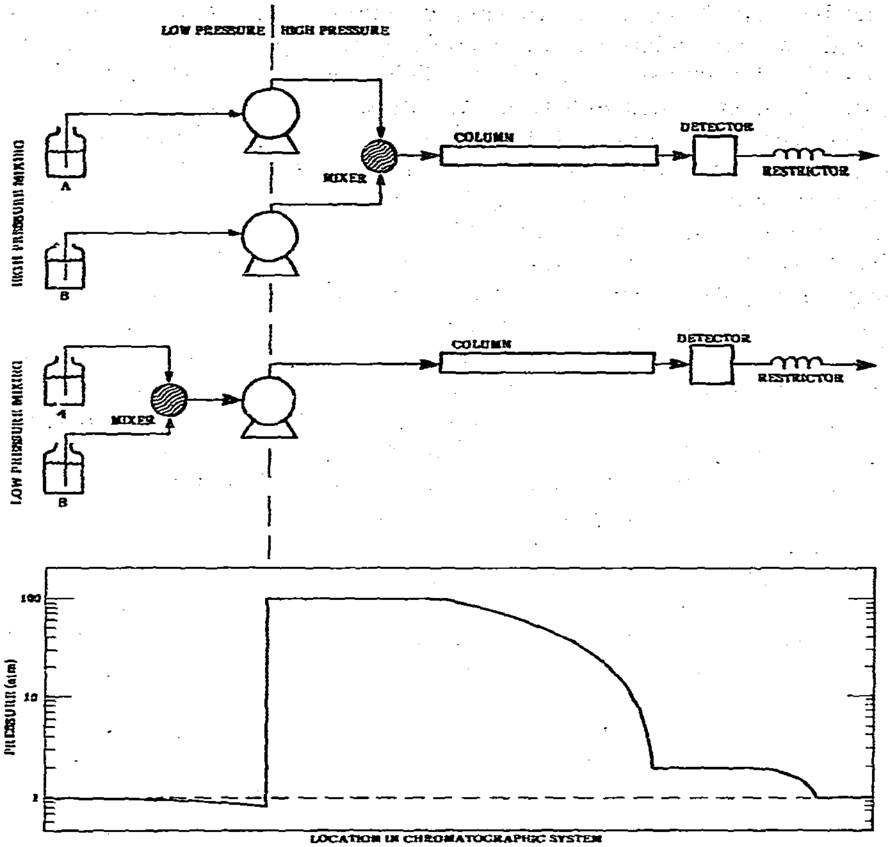


Fig. 5. Comparison of one-pump and two-pump architectures. The upper system represents a two-pump, high-pressure-mixing system such as the SP 3500B. The lower system represents a one-pump, low-pressure-mixing system such as the SP 8000. The pressure drops appear non-linear along the column length only because it is a semi-logarithmic plot.

Williams and Miller[31] compared several techniques for purging water: dynamic and static vacuum, with and without manual and ultrasonic agitation; ultrasonic treatment alone; and purging with an inert gas. The most effective system tested was inert gas purging at flow-rates of about 1000 ml/min of 100-ml water samples. This technique removed 95–98% of the dissolved oxygen in 15–30 sec, where the next best technique of dynamic vacuum with agitation took 1–2 min to remove the same quantity of gas.

The degassing technique we used was that employed by the SP 8000 chromatograph. This has been briefly described only once[10] and is the subject of a patent application. The method uses helium to sparge all pure solvents (up to three in the ternary-type mobile phase control system of the chromatograph). It was found that this is the only gas, with the possible exception of neon, which is capable of eliminating all the previously mentioned problems. That is, it not only prevents bubble formation but eliminates all gases except helium from the mobile phase. (There is no literature on the helium solubility in binary mixtures.) Our experimental evidence suggests two possible explanations for this. The solubility curve for helium may be non-linear, like the oxygen shown in Fig. 3. But the amount of gas involved may be so low, *i.e.*, the absolute value of the gas volume which is supersaturated may be so small, that the microbubbles formed do not manifest themselves. Alternatively, the solubility curve may be nearly linear, leading to only small amounts of gas which are above the saturation level. Both of these may be operating.

The effectiveness of this technique for eliminating bubble generation during low-pressure mixing is illustrated in Fig. 6. This plots the volume of air evolved per ml of mobile phase formed by mixing two pure, air-saturated solvents. A Model 740B pump (dual reciprocating piston, feedback-controlled type) was used for each solvent. The outputs of the pumps were teed together and the tee exit line directed to a 1.0-ml mixing chamber. The position of the inlet and outlet lines, and the shape of the "roof" of the chamber were designed to trap any bubbles formed. After passage of a measured amount of total mobile phase through the chamber at a pre-determined solvent composition, the gas bubbles formed were sucked into a precision syringe which was connected to the top of the chamber. Replicate runs were not made, so the detailed shape of the curves is not to be taken as significant. Considerable scatter was suspected. The general shape, however, is no doubt accurate. These curves correspond well to the area of supersaturation in Fig. 3. Note that the more similar the two solvents, the less gas was evolved. The hexane–isooctane run produced no bubbles. In all cases, no bubbles were observed when the two solvents were helium degassed.

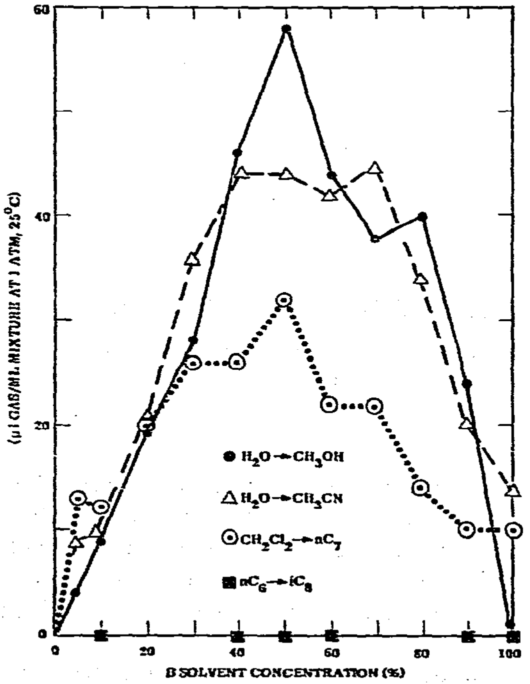


Fig. 6. Gas evolved *vs.* solvent composition. Apparatus and procedure described in text.

UV absorbance of dissolved gases

During the above studies of gas solubility and degassing techniques, we noticed that UV detector baselines sometimes drifted considerably when degassing was initiated. We have experimentally confirmed that this is due to the presence of oxygen, as illustrated in Fig. 7. It is a record of UV detector signal at 254 nm and 0.08 AUFS for a 1.0-cm cell with methanol flowing. The trace starts with the baseline after the methanol has been sparged with pure oxygen for some time. A stable signal was obtained. Then the sparging gas is changed to air, and the signal drifts down to a new equilibrated value. Then the gas is switched to helium. Yet another level is found. The ratios of these three signals are: (helium–air–oxygen) 0:0.223:1.00. The ratio of partial pressures, *i.e.*, the theoretical signal levels if due to oxygen concentration, are 0:0.209:1.00. This represents a 6.7% error from theory.

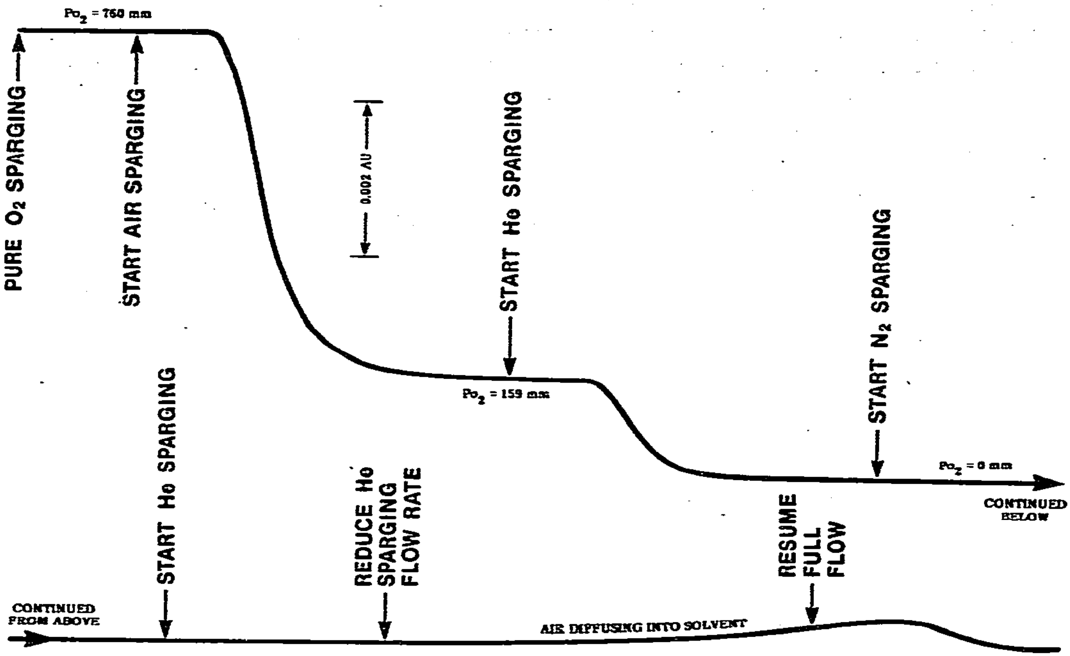


Fig. 7. UV detector standing signal *vs.* oxygen concentration in mobile phase. Solvent, methanol; flow-rate, 2.0 ml/min; pressure, nominally 1 atm; temperature ambient (approximately 25 °C); detector, Model SP 8200 at 254 nm with a 1-cm path cell.

The gas is further changed from helium to nitrogen and back to helium. The stable baseline is consistent with the hypothesis that it is the oxygen only which is responsible for the signal. Finally, the sparge rate was reduced, allowing air to back diffuse through the vent tube into the solvent bottle. The upscale drift due to oxygen absorbance is evident. Re-establishment of an adequate sparge rate rapidly brings back baseline stability.

The amount of absorbance varies considerably among the common chromatographic solvents, as shown in Fig. 8. The UV absorbance at 254 nm was monitored at a sensitivity of 0.02 AUFS. Note that water exhibits only a very small effect at this wavelength, whereas the tetrahydrofuran baseline changed more than 0.16 AU. The baseline shifts are completely reversible; resumption of air sparging elevates the signal back to the original level. Evans[32,33] and Munck and Scott[34] demonstrated that dissolved oxygen gives rise to such absorption in the far UV in a number of organic solvents. This was observed for *n*-hexane, *n*-heptane, methanol, ethanol, diethyl ether and cyclohexane. The absorbance was found to be directly proportional to the partial pressure of oxygen above the solution. The absorbance increases at shorter wavelengths. Comparing the absorbance of the amount of oxygen dissolved in the solvent with the absorbance of an equivalent concentration of gaseous oxygen (negligible at the wavelengths examined) leads to a conclusion that the absorption of the solution must be due to interaction between oxygen and the solvent.

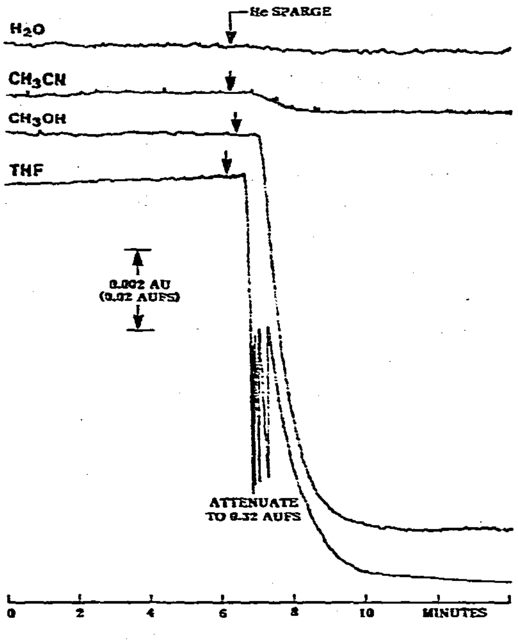


Fig. 8. UV detector standing signal with and without degassing for various solvents. Solvent, as indicated; flow-rate, 15 ml/min (splitter in front of detector providing 5 ml/min detector flow); pressure, 1 atm in solvent reservoir, 2 atm at pump outlet; temperature 23 ± 0.5 °C; detector, Model SP 8310 at 254 nm with a 0.6-cm path cell.

Heidt and Ekstrom[35,36] have examined this phenomenon in water. The absorption coefficient, ε, was independent of oxygen concentration, increased with decreasing wavelength, and increased with increases in temperature. They explained the results in terms of the existence of two different hydrates of molecular oxygen in water. Pure (deoxygenated) water also was found to absorb UV light and behave in a similar manner, but the magnitude of the effect was very much less than the light absorption due to molecular oxygen in water.

Thus dissolved oxygen affects HPLC mobile phases in two ways, one of which is reversible, the other non-reversible. The reversible effects have been described above and are due to the absorbance of molecular oxygen itself (small) and to the absorbance of the molecular complex between oxygen and the solvent (large). Removal of oxygen gives rise to a decrease in UV detector baseline signal with this effect. The non-reversible effects are caused by the interaction of oxygen with the solvent to form relatively stable chemical species. The cyclic ether tetrahydrofuran (THF) appears to be particularly bad in this respect, as it is thought to form a hydroperoxide and a series of unstable peroxides. Fig. 8 has shown that the reversible effect with THF is also large.

Fluorescence effects of dissolved gases

The role of oxygen in fluorescence systems is quite complex and has been the subject of debate and experiment for many years. An early publication on the role of oxygen in fluorescence quenching was published by Bowen and Williams[37] who discussed in particular the quenching of aromatic hydrocarbon fluorescence. Later workers[38,39] found that the quenching effect of oxygen usually followed the Stern Volmer relationship $F_0/F = 1 + K[O_2]$. Results reported by Parker and Barnes[39] for the quenching of the borate–benzoin complex show that at 0.1% (v/v) oxygen in nitrogen in equilibrium with the solvent, ethanol, an 8% error occurs. At 0.8% oxygen the fluorescence is reduced 43%, and with air the fluorescence intensity is reduced 94%. The same authors showed that the majority of the effect was reversible, but that there was a second, slower reaction which was irreversible.

Bar and Weinreb[38] showed that in considering the mechanism of oxygen quenching, the mechanism of excitation is important. If the system is such that the solvent is absorbing the exciting radiation, and the energy is transferred to the solute, quenching occurs by competition between the oxygen and the solute. They report that as the concentration of solute decreases, the quenching effect of oxygen increases. With systems where the solute absorbs the exciting wavelength directly and the solvent does not absorb, oxygen quenching is again more efficient at lower concentrations but the magnitude of the effect with concentration is not so great. This is postulated to be owing to competition between oxygen quenching and self quenching, which increases considerably with increasing solute concentration.

That the effect of quenching is specific to oxygen was confirmed by Furst *et al.*[40], who examined the fluorescence of a large number of compounds in solutions saturated with oxygen, nitrogen, argon, carbon dioxide, hydrogen and nitrous oxide. All gases except oxygen gave the same fluorescence intensity. Thus, the effect of the other gases is to remove oxygen from the solution without otherwise affecting the fluorescence.

The quenching effect varies with compound type, as was briefly mentioned in the introduction. Aromatic hydrocarbons, aliphatic aldehydes and ketones are particularly susceptible to oxygen quenching, whereas substituted aromatics and some heterocyclics are much less susceptible.

Clearly, the analyst using HPLC with fluorescence detection must be concerned with the variation of the magnitude of the quenching effect among different compounds, and in the non-linear character of this effect. This is particularly true when working at the trace level, where the limits of the detector are being stretched, and the oxygen quenching is at its most efficient.

UV and fluorescence effects in chromatography

Fig. 9 shows the effect of dissolved oxygen on both the detector baseline and the eluted peak response (height and area) for both UV and fluorescence detectors. The data, made on a dual channel recorder, was collected by repetitively injecting the one-peak sample every 1.8 min using the SP 8000 autoinjector. Initially, the mobile phase was helium degassed. At time 0, the helium was replaced by an air sparge. After 16 min, the helium degassing was resumed. The conditions are listed in the figure caption.

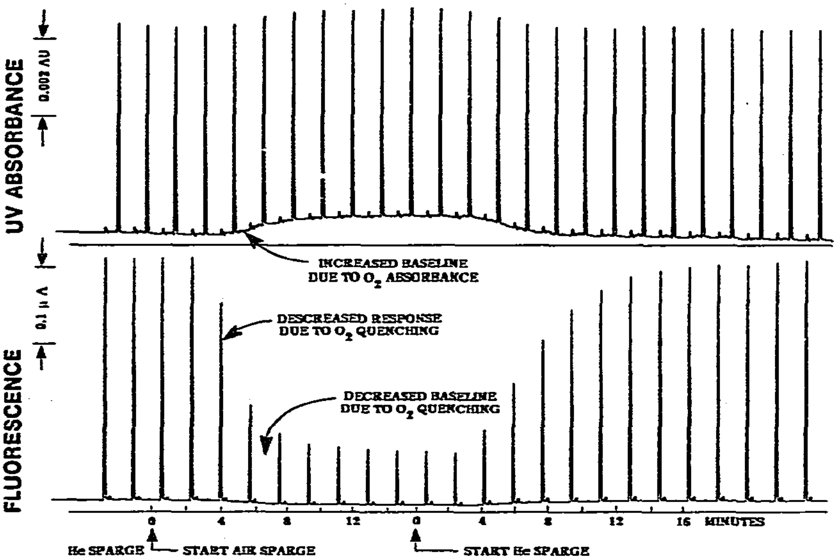


Fig. 9. UV absorbance detector and fluorescence detector response to mobile phase oxygen. Column 250 × 4.6 mm I.D.; packing, 10-μm LiChrosorb RP-8; solvent, water–acetonitrile (25:75); flow-rate, 5.0 ml/min; temperature, 25 °C; detector, Model SP 8310 UV detector at 254 nm with a 1.0-cm path cell, and Model SP 770 fluorescence detector at 250 nm exciting wavelength and with 340 nm emission wavelength filter, 1.0 μA full scale; sample size, 10 μl; sample, naphthalene.

The UV detector trace exhibits the baseline elevation previously described in association with Figs. 7 and 8. However, the response to the compounds does not change.

The fluorescence detector trace also exhibits a baseline shift. This has not yet been mentioned. The change is in the opposite direction to the UV drift. This is because the increased concentration of oxygen quenches the background fluorescence of the mobile phase, whereas in the UV detector the oxygen is responsible for increased absorbance. The magnitude of this drift is noteworthy. It is about 0.004 μA, or about 40% of the full-scale sensitivity of the detector (0.01 μA full scale). However, the most marked effect of the oxygen is in the sample response, which is only about 20% of that when the solvent is degassed.

Fig. 10 also shows these effects, as well as a number of general characteristics of the two detectors. Four separate chromatographic runs were made, using both a UV and a fluorescence detector on each run. Thus there are eight chromatograms.

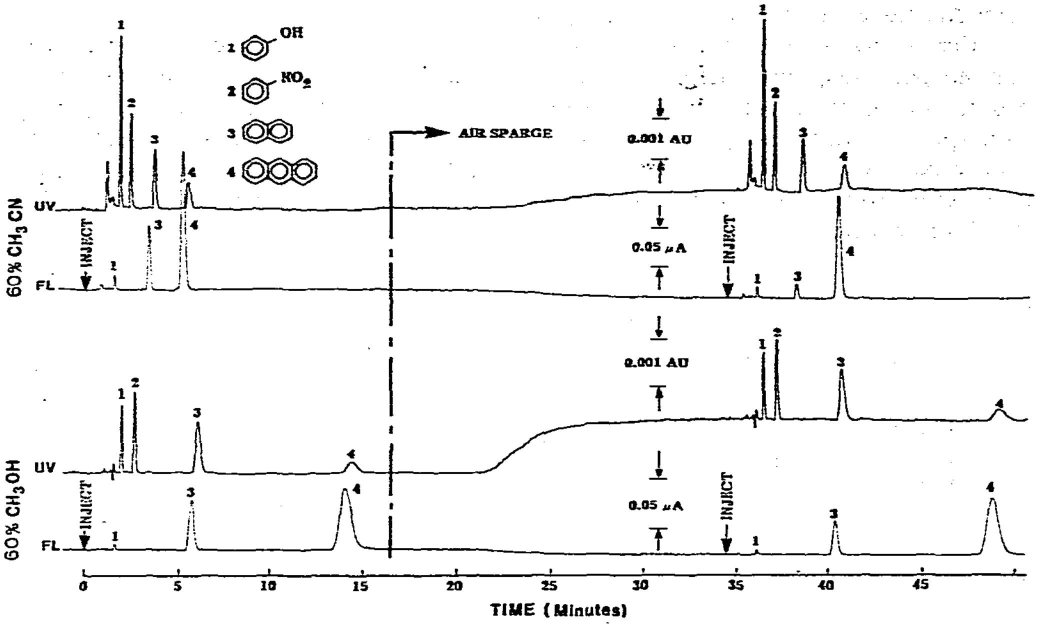


Fig. 10. Characteristics of UV and fluorescence detectors. Column, 250 × 4.6 mm I.D.; packing, 10-μm LiChrosorb RP-8; solvent, water–acetonitrile (40:60) and water–methanol (40:60); flow-rate, 3.0 ml/min; temperature, 25 °C; detector, same as Fig. 9, except UV at 0.01 AUFS and fluorescence at 0.5 μA full scale; sample size, 10 μl; sample, as shown.

The upper four chromatograms are run with a mobile phase of 60% acetonitrile in water. The bottom four chromatograms are run under identical conditions, except the mobile phase is 60% methanol in water. The four chromatograms on the left were made using helium-degassed mobile phases. The four chromatograms on the right were made using air sparged (air saturated) mobile phases. A vertical line indicates the point at which the gases were changed. The many aspects of the complex behavior of these two detectors are described below.

UV and fluorescent detector response differences

The upper left chromatograms illustrate the well known fact that the two detectors respond quite differently to different compounds. Solute 2, nitrobenzene, is not even detected by the fluorescence detector under these conditions. These two chromatograms will serve as a reference against which the other three sets will be compared.

Response differences caused by the solvent

The lower left chromatograms are quite different. First, quite obviously because the peaks are more retained. But a close inspection shows that, for some compounds, the detector response has changed. This is true for both detectors. The solvent composition of the mobile phase thus has a profound effect on response.

Baseline and response changes caused by dissolved oxygen

The upper right chromatograms, compared to the upper left ones, show the effects of oxygen. UV detector: baseline change but no peak height or area change. (For a description of the dependence of peak height and area on mobile phase composition, see ref. 41) Fluorescence: baseline change and peak height and area change. Note that peak 3 has been affected much more than peak 1. Thus an internal standard does not solve the problem. The sensitivity of the fluorescence detector has been reduced for all peaks, although only slightly in the case of peak 1.

The lower right chromatograms, compared to the lower left ones, show similar but not identical effects of oxygen on the fluorescence detector. Note for example that there is much less change in the relative sizes of peaks 1 and 3, compared to the upper (acetonitrile) chromatograms.

Other effects of dissolved gases

Two major effects of dissolved gases have not yet been mentioned: the changes in refractive index caused by changes in concentrations of various gases, and the changes in pH caused by changes in the concentration of carbon dioxide in unbuffered mobile phases. These effects will be discussed in subsequent papers, but a few comments will be made here.

The refractive index of the mobile phase is a function of the types and concentrations of dissolved substances, including gases. The effects of gases are small, but it is likely that, under some circumstances, careful attention to controlling dissolved gases will produce more stable refractive index detector baselines, in effect improving sensitivity.

The pH of the mobile phase is an important retention variable. Since dissolved carbon dioxide brings the pH 7.0 of pure water down to about 5.5, changing carbon dioxide levels are expected to effect retention times of basic compounds. UV and fluorescence detector response is also a function of pH, since the molar extinction coefficient is often pH dependent. Experiments of the type shown in Fig. 10 are expected to reveal such effects readily, when appropriate sample types are chosen.

CONCLUSIONS

We have demonstrated that gases dissolved in the mobile phase play a complex role in HPLC. Their non-linear solubility behavior in binary mixtures tends to cause the formation of gas bubbles when solvents are mixed, a process which degrades pump and detector performance.

Whereas the gas bubble problem has its solution in the reduction of the concentration level of all gases, most of the other problems can be dealt with by controlling just the oxygen concentration. Oxygen affects the standing signal levels of both UV and fluorescence detectors. It also affects the response characteristics of the latter. This is a complex phenomenon involving solute type, mobile phase solvent composition and oxygen concentration. Much work remains to be done before we will understand what is happening. In spite of limited understanding of the mechanisms, one can at least attempt to hold the oxygen level constant so as to provide reproducible chromatographic results. The most effective constancy is to take the oxygen concentration to zero.

The effect of dissolved gases on the performance of refractive index detectors is yet to be explored, as are the consequences of varying carbon dioxide concentrations on solute retention and on detector response characteristics. The techniques discussed here can be readily applied to such studies.

Much remains to be learned about gas solubility, and no doubt the main source of such knowledge will be the continued use of gases as probes to study the structure of liquids. The increasing use of ternary mixtures in both isocratic and gradient separations provides an even more difficult theoretical problem. In any event, there are a variety of techniques available for controlling gas concentrations and thereby eliminating problems which would otherwise exist. The new helium degassing method described appears to be a particularly simple and effective method.

NOTE ADDED IN PROOF

Subsequent to the submission of this paper, R. W. Cargill sent us a pertinent private communication. His data will be published in *J. Chem. Soc., Faraday Trans. I* (1978). It indicates that the solubility behavior of helium in aqueous alcohol mixtures is very similar (non-linear) to that shown in Fig. 2 for oxygen, although the magnitude of the solubility is lower. We had postulated two explanations of why helium degassing eliminates bubble problems (see the "gas control methods" section). The Cargill data suggests that the low-solubility postulate is correct, and not the linear-behavior postulate. The Cargill paper also makes a significant contribution to the understanding of water structure, and will be of interest to those who are working to elucidate retention mechanisms in reversed-phase liquid chromatography.

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