The Solubility of Nitrogen and Air in Liquids

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This review covers the solubility of nitrogen and air in liquids as a function of temperature and pressure. Solubility data for individual systems were critically evaluated. Recommended or tentative values are presented as smoothing equations and/or in tabular form. Trends in homologous series or related solvents are discussed. Data for the *n*-alkanes were smoothed with respect to temperature, pressure, and carbon number. Liquids include: water; heavy water; seawater; aqueous salt solutions; mixed solvents; hydrocarbons; organic compounds containing oxygen, halogen, sulfur, nitrogen, or silicon; olive oil; various biological fluids; H_2S; SO_2; NH_3; CO_2; nitrogen oxides; and several halogen and boron containing inorganic solvents.

Key words: air; aqueous solutions; biological fluids; gas solubility; hydrocarbons; inorganic solvents; mixed solvents; nitrogen; organic solvents; seawater; water.

Contents

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List of Tables

List of Figures

1. Introduction

In this review, we are concerned with the solubility of nitrogen and air in most liquids for which data are available and over all temperatures and pressures. The fluids considered include pure liquids, organic and inorganic solvents, mixtures, biological fluids, and miscellaneous fluids. We did not include molten salts, alloys, metals, glasses, and slags or polymeric materials. For the systems included, there is a considerable literature at elevated pressures.

The literature beginning with the pioneering work of Henry in 1803 was systematically searched and the coverage includes papers published through 1981. Not all papers with relevant solubility data will be discussed or cited since this is a critical review. Only papers containing data which are sufficiently precise or are significant for other reasons are cited. For comprehensive coverage, see Ref. 1. We would appreciate hearing about papers we missed or other oversights.

Other sources to consult are Markham and Kobe[2] (general review through 1940); Battino and Clever[3] (general review through 1966); Clever and Battino[4] (general review through 1974—a chapter); Wilhelm and Battino[5] (thermodynamic functions at 298.15 K for 16 gases in 39 solvents plus seven fluorocarbon gases in eight solvents); Wilhelm, Battino, and Wilcock[6] (review on low-pressure solubility of some 57 gases in water); Gerrard's two books[7,8] (emphasizing the "R-line" analysis and containing some comprehensive annotated surveys); Kertes, Levy, and Markovits[9] (chapter—a general review); Stephen and Stephen[10] (data tables); Linke (Seidell)[11] (data tables); Landolt/Börnstein Tabellen[12] (data tables and graphs with critical evaluation); the International Critical Tables[13]; the IUPAC volume on nitrogen and air solubilities[1]; and the published volumes of the IUPAC Solubility Data Series for critically evaluated data on the solubility of other gases. Our previous paper for this journal[14] was on oxygen and ozone solubilities. Finally, the books by Prausnitz[15] and by Hildebrand, Prausnitz, and Scott[16] contain excellent chapters on gas solubilities.

There is a gray area at high pressures where the systems can be considered to be examples of vapor–liquid equilibrium or gas solubility. The systems analyzed in this paper were considered to be examples of gas solubilities, but other choices could have been reasonably made.

Daniel Rutherford is usually considered to be the discoverer of nitrogen (1772). Important experiments on this "phlogisticated" air (contrasted with "dephlogisticated" air or oxygen) were carried out by Priestly, Scheele, and Cavendish. The name azote (from the Greek, meaning without life) was given to the gas by Lavoisier. The English name is nitrogen because of its presence in niter or nitre (KNO_3). Nitrogen forms 78.09% of the atmosphere by volume and 75.51% by weight. However, it is present only to the extent of 0.0046 wt. % in the igneous rocks of the crust of the earth. Its content in seawater is negligible.

2. Methods of Measurement

Methods of measuring the solubility of nitrogen in liquids are not unique to this gas. Therefore, methods will not be discussed other than generally in this brief section. Most gas solubilities are determined via physical means using manometers, burets, and calibrated volumes with the apparatus thermostatted in some manner. Gas chromatography has been used, but the precision is of the order of 3% or poorer. The apparatus developed by Benson and Krause[17] and also in use in this laboratory is capable of precisions of hundredths of a percent. However, it is rare to find published data of precision better than 1%.

Methods of measuring gas solubility are discussed in Refs. 2–4 and 9. Reference 1 contains a brief description for each paper cited there. The original papers can, of course, also be consulted.

3. Treatment of Solubility Data

The reviews[2–4,9] discuss solubility units and how they are derived and interrelated. The gas solubility volumes in the Solubility Data Series contain a section on units. The nitrogen and air volume[1] also contains a paper by E. Wilhelm on thermodynamic considerations on gas solubilities, presenting a rigorous thermodynamic treatment on solubility; as well as a paper by H. L. Clever on the Sechenov salt-effect parameter discussing forms of expression and interconversion. Clever[1] also includes an historical note on I. M. Sechenov. The special approach using the "R-line" used by Gerrard is outlined in his two books.[7,8]

3.1. Solubility Units

Over the years, gas solubilities have been expressed in a bewildering variety of units, some of them specific to a specialized research area. We have chosen to present solubilities as the mole fraction at 0.101 325 MPa partial pressure of gas (or other pressure where specified) and also as the Ostwald coefficient L_v°. In some cases where it was difficult to convert to these solubility units, we present the original data. In a few cases, for the convenience of the user, we present data in specialized units.

Since converting units has taken up a significant portion of the preparation time of this manuscript, we recommend that authors present their solubility data as mole fractions (at a specified pressure) or Ostwald coefficients as defined below. (The senior author has a paper[183] in preparation on the nature of the Ostwald coefficient.)

The Ostwald coefficient L_v°, to be consistent with the senior author's notation, is defined as

$$L_v^\circ = (V_g / V_1^\circ)_{equil}, \tag{1}$$

where V_g is the volume of gas absorbed by the volume V_1° of pure liquid (not solution) both measured at equilibrium at the temperature of the experiment. If the gas behaves ideally (within experimental error) and if Henry's law is applicable for the experimental conditions, then the Ostwald coefficient as defined above is independent of the partial pressure of the gas. It is important that the actual pressure conditions of the experiment be specified, specifically whether total pressures or partial pressures were measured.

The mole fraction may be calculated from the Ostwald

Table 1. Second virial coefficients for nitrogen

T/K	$B_{11}/cm^3 \, mol^{-1}$	Per cent Error	T/K	$B_{11}/cm^3 \, mol^{-1}$	Per cent Error
100	-160	1.9	300	-4.2	0.02
150	-71.5	0.58	400	9.0	0.03
200	-35.2	0.21	500	16.9	0.04
250	-16.2	0.08			

coefficient via

$$x_1 = \left[\frac{1}{V_1^\circ L_v^\circ} \left(\frac{RT}{P_1} + B_{11} \right) + 1 \right]^{-1}, \tag{2}$$

where V_1° is the molar volume of the pure liquid at the Kelvin temperature T, P_1 is the partial pressure of the gas, R is the gas constant, and B_{11} is the second virial coefficient of the gas. B_{11} values for nitrogen[18] are given in Table 1. Except for the most precise measurements the correction for nonideality in Eq. (2) is negligible in the range 250 to 500 K.

The Bunsen coefficient α is frequently used. It is defined as the gas volume at STP (0.101 325 MPa and 273.15 K) absorbed per volume of pure liquid at the temperature of the measurement. The Bunsen coefficient is related to the Ostwald coefficient by

$$\alpha = 273.15 L_v^\circ /(T/K). \tag{3}$$

The general formulation of Henry's law in terms of the mole fraction is

$$p_1 = K_H x_1, \tag{4}$$

where K_H is the Henry's law constant (or the Henry coefficient) and p_1 is the partial pressure of the gas. Henry's law is strictly speaking a limiting law (for $p \to 0$) although in its simple form as in Eq. (4) it has been shown to be applicable over quite remarkable pressure ranges. See Wilhelm's article in Ref. 1 for the rigorous thermodynamic treatment involving Henry's law. Gerrard has vociferously argued against the use and validity of Henry's law and his arguments are ably put forward in Refs. 7 and 8. Since there is much pressure dependent solubility data available for nitrogen, you can get a rough check of its usefulness in the coefficient of $\ln(P/\text{MPa})$ when $\ln x_1$ is fit against this pressure term later in this paper for many different systems over widely different pressure ranges. The coefficient of $\ln(P/\text{MPa})$ is invariably rather close to 1.0. Since Henry's law takes on different forms depending on the concentration unit used, the explicit form will be so identified where it differs from Eq. (4).

Any specialty units not described above will be discussed where they occur in the text. Where it was feasible to do so we converted original solubilities to mole fraction and/or Ostwald coefficients. SI is used throughout.

3.2. Reliability Estimates

We have estimated the precision of the data used in this paper using authors' statements, comparison with other workers, and in the final analysis our own judgment. Precisions are reported in terms of one standard deviation in $\ln x_1$ or x_1 (these are specified in the text) unless otherwise noted.

3.3. Fitting Equations

The general equation used for fitting the data is the following where $\tau = T/100$ K:

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + A_3 \tau + B_0 \ln(P/\text{MPa})$$

$$+ B_1(P/\text{MPa}) + B_2(P/\text{MPa})^2 + C_0 C. \tag{5}$$

The A terms are used for temperature dependent data, the B terms for pressure dependent data, and C is the number of carbon atoms in a homologous series. For any given set of data, we used the smallest number of terms consistent with minimizing the standard deviation.

The SAS statistical package[19] was used for most of the data processing. The RSQUARE routine was particularly useful since one can put in all possible terms on the right-hand side of Eq. (5) and receive a listing of the r-square values for all possible permutations of those terms. We then had a basis for guiding our judgment as to which set of terms made most sense for trying for that particular system. The SAS package provided all standard statistical values. The use of this package made it possible for us to easily fit solubility data to temperature and pressure, and also to temperature, pressure, and carbon number for homologous series. However, our attempt to smooth data over very wide temperature and pressure ranges occasionally resulted in anomalous results such as smoothed mole fractions greater than one. Of course, these values are only an artifact of the fitting process.

For the convenience of the reader we present in many instances tables of smoothed data as well as the fitting equation.

3.4. Thermodynamic Functions

By taking the appropriate derivatives of just the temperature dependent portion of Eq. (5), i.e., $C = 0$ and the constant A_0 modified by the addition of the pressure terms for $P = 0.101\ 325$ MPa or with no pressure terms but the pressure at 0.101 325 MPa, the thermodynamic functions may be calculated according to:

$$\Delta \overline{G}_1^\circ = -A_0 R (T/K) - 100 A_1 R$$

$$- A_2 R (T/K)\ln \tau - A_3 R (T/K)^2/100, \tag{6}$$

$$\Delta \overline{S}_1^\circ = A_0 R + A_2 R \ln \tau + A_2 R + 2A_3 R\tau, \tag{7}$$

$$\Delta \overline{H}_1^\circ = -100 A_1 R + A_2 R (T/K) + A_3 R (T/K)^2/100, \tag{8}$$

$$\Delta \overline{C}_{p_1}^\circ = A_2 R + 2A_3 R\tau. \tag{9}$$

(Recall that $\tau = T/100$ K.) These thermodynamic functions refer to the change in the property upon transfer of gas from the vapor phase at 0.101 325 MPa partial pressure of gas to the (hypothetical) solution phase of unit mole fraction. The temperature dependance usually needs only two constants using the $1/\tau$ term or the $\ln \tau$ term. Occasionally, both terms were needed. Pressure dependance generally required only the $\ln (P/\text{MPa})$ term.

4. Nitrogen Solubilities

The solubility of nitrogen in liquids will be covered in this section starting with water. Where applicable the low

pressure (usually at 0.101 325 MPa) work is discussed first. This is then followed by the high pressure work which also includes smoothing functions (again, where applicable) covering the entire range of pressures and temperatures. Homologous series are treated separately. Air solubilities are covered in Sec. 5.

4.1. Solubility of Nitrogen in Water

Since the early investigations by Bunsen,[20] the solubility of nitrogen in water has been the subject of numerous investigations. Due to widely ranging temperature and pressure conditions, the data are presented in three groups:

(1) temperatures up to 350 K (low pressure);
(2) temperatures above 350 K (high pressure); and
(3) isotope studies.

4.1.a. Temperatures up to 350 K (Low Pressure)

Data from studies with temperatures below 350 K and pressures about 0.101 325 MPa were fitted to Eq. (5). Data falling more than 2 standard deviations from the smoothed curve were excluded. A total of 73 points were finally selected from 9 sources: from Hufner,[21] 1 point; from Fox,[22] 18 points; from Bohr,[23] 1 point; from Hawkins and Shilling,[24] 1 point; from Morrison and Billet,[25] 10 points; from Clever et al.,[26] 1 point; from Klots and Benson,[27] 28 points; from Farhi et al.,[28] 6 points; and from Murray et al.,[29] 8 points.

The best statistically justifiable fit utilized the first three terms in Eq. (5), and resulted in

$$\ln x_1 = -67.387\,65 + 86.321\,29/\tau + 24.798\,08\ln \tau.$$
$$(10)$$

At the middle of its temperature range, Eq. (10) had a stan-

Table 2. Solubility of nitrogen in water for partial pressure of gas of 0.101325 MPa calculated by Eq. (10)

T/K	$v^0/\text{mL mol}^{-1}$ [a]	$10^5 x_1$	$10^2 L$
273.15	18.018	1.908	2.373
278.15	18.016	1.695	2.147
283.15	18.020	1.524	1.965
288.15	18.031	1.386	1.818
293.15	18.047	1.274	1.698
298.15	18.068	1.183	1.601
303.15	18.094	1.108	1.523
308.15	18.123	1.047	1.461
313.15	18.156	0.9981	1.413
318.15	18.193	0.9585	1.376
327.15	18.233	0.9273	1.349
328.15	18.276	0.9033	1.331
333.15	18.323	0.8855	1.321
338.15	18.372	0.8735	1.319
343.15	18.425	0.8666	1.324
348.15	18.480	0.8644	1.336

[a]From: Ref. 30.
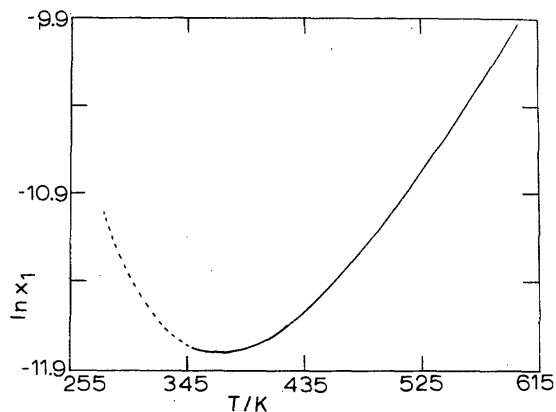
FIG. 1. Mole fraction solubility of nitrogen in water at 0.101 325 MPa and 350–600 K.

dard deviation of 0.72%. Values calculated by Eq. (10) are listed in Table 2. Values for the molar volume of pure water were included to facilitate conversion to other solubility units.

Figure 1 gives the smoothed curve using a smoothing equation developed by Clever and Han[182] for nitrogen solubilities in water from 350 to 600 K and at 0.101 325 MPa. Their equation is

$$\ln x_1 = -55.0165 + 69.2199/\tau + 18.7292\ln \tau. \quad (10a)$$

The thermodynamic functions for the transfer of gas from a pressure of 0.101 325 MPa into hypothetical unit mole fraction solution were calculated from the coefficients in Eq. (10) according to Eqs. (6)–(9). Values for the molar Gibbs energy, enthalpy, and entropy changes are given in Table 3. Note that for the three term fit using Eq. (10) that $\Delta C_{P_1}^{\circ}$ has a constant value of 206 J mol^{-1} K^{-1} within the precision of the data in this temperature region.

The large positive values for $\Delta \overline{G}_1^{\circ}$ that increase with

Table 3. Thermodynamic functions for the process of dissolving nitrogen at 0.101325 MPa partial pressure in water at selected temperatures

T/K	$\Delta \overline{G}_1^{\circ}/\text{kJ mol}^{-1}$	$\Delta \overline{H}_1^{\circ}/\text{kJ mol}^{-1}$	$\Delta \overline{S}_1^{\circ}/\text{J mol}^{-1}\text{K}^{-1}$
273.15	24.68	-15.45	-147
278.15	25.41	-14.42	-143
283.15	26.11	-13.39	-140
288.15	26.80	-12.36	-136
293.15	27.47	-11.33	-132
298.15	28.12	-10.30	-129
303.15	28.76	-9.27	-125
308.15	29.38	-8.24	-122
313.15	29.98	-7.21	-119
318.15	30.57	-6.17	-115
323.15	31.14	-5.14	-112
328.15	31.69	-4.11	-109
333.15	32.23	-3.08	-106
338.15	32.75	-2.05	-103
343.15	33.26	-1.02	-100
348.15	33.75	0.01	-97

increasing temperatue reflect the low solubility of nitrogen in water and its decreasing solubility with increasing temperature. For new data see Ref. 184.

4.1.b. Temperatures above 350 K (High Pressures)

The solubility of nitrogen at temperatures above 350 K and pressures up to 100 MPa has been examined by several researchers. The following equation was used to fit their data in terms of both temperature and pressure:

$$\ln x_1 = -43.0160 + 48.5244/\tau + 13.9321 \ln \tau$$
$$+ 0.970\,040 \ln (P/\text{MPa})$$
$$- 0.000\,482\,96(P/\text{MPa}). \tag{11}$$

Data falling more than two standard deviations from a smoothed curve were eliminated. The remaining data were from Goodman and Krase,[31] 19 points; from Wiebe et al.,[32] 32 points; from Saddington and Krase,[33] 17 points; and from O'Sullivan and Smith,[34] 18 points. The standard deviation in this data was 0.056, or about 5% of a typical value. The standard deviation of the fit in $\ln x_1$ is 0.057.

4.1.c. Isotope Effects/Heavy Water

Little work has been done on the effect of isotopes on the solubility of nitrogen in water and these results are tentative. Klots and Benson[35] determined the solubility of $^{28}N_2$ and $^{29}N_2$. The ratio of Henry's law constants was $1.000\,85 \pm 0.000\,10$, with the heavier isotope being more soluble in water.

Cosgrove and Walkley[36] reported the solubility of nitrogen in D_2O between 278 and 313 K. At a nitrogen partial pressure of 0.101 325 MPa, the corresponding mole fractions ranged from 10% to 7% higher in D_2O than H_2O. Their data are represented by

$$\ln x_1 = -71.371 + 91.786/\tau + 26.766 \ln \tau, \tag{12}$$

with a standard deviation of 0.0074 in $\ln x_1$. Smoothed data are presented in Table 4.

Table 4. Solubility of nitrogen in D_2O at 0.101325 MPa

T/K	$10^5\,x_1$
278.15	1.685
283.15	1.516
288.15	1.380
293.15	1.270
298.15	1.182
303.15	1.110
308.15	1.052
313.15	1.006

Table 5. Coefficients for Eq. (13) for several solubility units and reference conditions for nitrogen solubility in seawater

Coefficient	Bunsen Coefficient[a] α	mL N_2(STP)[b] Liter seawater	μmol N_2[b] kg seawater
A'	59.7745	-29.1410	-29.2710
B'	-76.7685	53.3161	58.6753
C'	-88.3270	7.499	10.3401
D'	19.5287	1.8298	1.5045
E'	7.1485×10^{-3}	7.365×10^{-3}	7.116×10^{-3}
F'	-3.9793×10^{-2}	-4.038×10^{-2}	-4.186×10^{-2}

[a] Nitrogen partial pressure of 0.101325 MPa.

[b] Nitrogen partial pressure that of water saturated air at a total pressure of 0.101325 MPa.

4.2. Solubility of Nitrogen in Seawater

There are relatively few papers concerning the solubility of nitrogen in seawater and they cover a wide range of salinity and temperature. Of these, the works by Douglas[37,38] and by Murray et al.[29] were chosen. In these sources, the temperature ranged from 271 to 307 K and the salinity ranged from 0 to 40 parts per thousand. The data from these different sources are reasonably consistent and of the same precision. A small correction to their published values for solubility was made by Chen[39] taking into account the change in liquid volume between degassed and gas-saturated seawater.

The results corrected by Chen were fit by the following equation:

$$\ln C = A' + B'/\tau + C' \ln \tau + D'\tau + E'S + F'S/\tau, \tag{13}$$

where τ is $T/100$ K, S is salinity in parts per thousand, and C is a measure of the solubility of nitrogen in seawater. Table 5 summarizes the coefficients for Eq. (13) when C is expressed in units of the Bunsen absorption coefficient, in mL of nitrogen at STP per liter of seawater, and in μmol of nitrogen per kg of seawater. The Bunsen coefficient values summarized in Table 6 are calculated via the fitting coefficients in Table 5 assuming a nitrogen partial pressure of 0.101 325 MPa. The other solubility units in Table 5 are more convenient for

Table 6. Bunsen coefficient, α, for nitrogen solubility in seawater at several temperatures and salinities

T/K	Salinity/parts per thousand				
	0	10	20	30	40
273.15	0.023678	0.021985	0.020413	0.018953	0.017598
278.15	0.020989	0.019539	0.018189	0.016933	0.015763
283.15	0.018805	0.017551	0.016380	0.015287	0.014267
288.15	0.017029	0.015932	0.014905	0.013944	0.013046
293.15	0.015584	0.014614	0.013705	0.012852	0.012052
298.15	0.014412	0.013546	0.012731	0.011966	0.011247
303.15	0.013466	0.012685	0.011949	0.011255	0.010602
308.15	0.012712	0.012000	0.011328	0.010693	0.010094

oceanographic purposes and are based on a total pressure of 0.101 325 MPa for all air components, including water vapor. The fitting of the data by Eq. (13) via any of the solubility units and reference pressure had a reproducibility of about $\pm 0.4\%$.

4.3. Solubility of Nitrogen in Aqueous Salt Solutions

The solubility of nitrogen in water is greatly influenced by the presence of electrolytes. This "salting-out" phenomenon is expressed quantitatively in the Sechenov (also spelled Setschenow) equation:

$$k_{scc} = (1/C_2)\log(C_1^{\circ}/C_1). \tag{14}$$

The units of k_{scc}, the salt-effect parameter, depend on the concentration units for C_2, the electrolyte concentration. The concentration of nitrogen in pure water is given by C_1°, while the gas concentration in the electrolyte solution is represented by C_1. Thus a positive salt-effect parameter indicates "salting-out" and a negative value results from the less common "salting-in."

The ratio of gas solubility in pure solvent and in electrolyte solution can be expressed in molar concentrations, Ostwald coefficients or Bunsen coefficients. These would be represented by k_{scc}, k_{scl}, and k_{sca}, respectively, and would be numerically equivalent. Alternate expressions of Sechenov salt-effect parameters include molality, mole fraction, and Kuenen coefficients. Conversion to these parameters may be made (see Clever's article in Ref. 1).

When $\log(C_1^{\circ}/C_1)$ is plotted against C_2 over a limited electrolyte concentration region, a constant value of k_{scc} may be determined. At higher concentrations, significant curvature can occur and the value of the Sechenov parameter will be concentration dependent.

Few independent studies on the effect of the same electrolyte on nitrogen solubility have been made. Consequently, whenever available, the authors' value for nitrogen solubility in pure water is used. This is necessitated due to the paucity of comparable data, plus there is the added benefit of cancelling systematic errors. The electrolytes are discussed

Table 7. Sechenov salt effect parameters for nitrogen dissolved in aqueous sulfuric acid solutions

H_2SO_4 Concentration/ mol L^{-1}	k_{scc} / L mol^{-1}	
	[23]	[40]
2.45	0.096	-
4.45	0.075	-
4.63	-	0.056
5.35	0.070	-
9.52	-	0.024
10.15	0.050	-
12.4	0.041	-
14.8	0.033	-
17.15	0.011	-
17.9	0.005	-0.002

Table 8. Sechenov salt effect parameters for nitrogen dissolved in aqueous sodium hydroxide solution (see comments in text)

T/K	k_{scc}/L mol^{-1}	T/K	k_{scc}/L mol^{-1}
273	0.20	373	0.16
298	0.22	398	0.19
308	0.19	423	0.25
323	0.22	475	0.20
348	0.16	513	0.14

in the following order: strong acids and bases, Group IA salts, Group II salts, and others.

4.3.a. Acids and Bases

Sulfuric acid is one of the few electrolytes whose solubility influence has been measured by several independent researchers. The results of Christoff[40] and Bohr[23] are summarized in Table 7 for $T = 294 \pm 1$ K and $P = 0.101$ 325 MPa. The salting-out effect decreases with increasing electrolyte concentration. At high concentrations, Christoff[40] found a small salting-in effect. A slight salting-in effect may have been observed for nitric acid by Shapka et al.,[41] but the data are inconclusive.

Sodium hydroxide is the only strong base for which a salt-effect parameter has been measured. Levina et al.[42] report widely scattered data which seem doubtful, especially at higher temperatures. See Table 8.

Table 9. Sechenov salt-effect parameters for nitrogen dissolved in aqueous sodium chloride solution

T/K	k_{scc}/L mol^{-1}	
278.15		0.175[b]
288.15	0.148[a]	0.150
298.15	0.129	0.134
308.15	0.117	0.122
318.15	0.109	0.115
328.15	0.106	0.111
338.15	0.106	0.109
348.15		0.110
358.15		0.112
368.15		0.115
378.15		0.119

[a]Mishnina [46], all values this column

[b]All values this column smoothed according to Eq. (15).

Table 10. Sechenov salt-effect parameters for nitrogen solubility in 1 molar LiCl and KI aqueous solutions

T/K	k_{scc} / L mol^{-1}	
	LiCl	KI
285.75	0.135	0.160
303.15	0.105	0.126
322.55	0.095	0.113
344.45	0.104	0.112

[a]Ref. 25.

4.3.b. Group IA Salts

The most widely measured salt-effect parameters for nitrogen are in aqueous sodium chloride solutions. Results from five groups are shown in Table 9. The data for the results of smoothed values shown in the third column come from Braun,[44] van Slyke et al.,[45] Morrison and Billett,[25] Mishnina et al.,[46] Smith et al.,[43] and O'Sullivan and Smith.[34] Mishnina et al.'s experimental results are shown for comparison. Higher temperature results by Morrison[25] and Smith[43] show a nearly constant value for k_{scc} up to 400 K. Clever[1] suggests the fitting equation

$$\ln k_{scc} = -47.878 + 70.050/\tau + 20.478 \ln \tau. \quad (15)$$

Table 10 shows the effect of lithium chloride and potassium iodide on nitrogen solubility as measured by Morrison and Billet.[25] Their potassium chloride results are widely scattered, with k_{scc} being 0.13 $\pm$ 0.04 L mol^{-1} for temperatures between 273 and 513 K.

A regular trend of salt-effect parameters as a function of cation and anion sizes for Group IA metal halides has been noted for oxygen solubility.[14] Specifically, the smallest cation-ion pair LiF had the largest value for k_{scc}, and these values decreased uniformly to the lowest value for the largest cation–anion pair CsI. No such trend is observed for nitrogen solubility. This may be due to less accurate measurements, fewer salts examined (four for nitrogen versus 20 for oxygen), or an actual chemical difference between the systems.

Other group IA salts investigated include Na$_2$SO$_3$ and Na$_2$SO$_4$. At 298.15 K, Yasunishi[47] calculated values for k_{scc} of 0.383 and 0.353, respectively. A mixture of the two electrolytes had a combined effect intermediate between these two values. No concentration dependence was observed from 0–1.0 mol L^{-1}.

Van Slyke et al.[45] determined the effect of 0.153 mol L^{-1} NaHCO$_3$ and 0.077 mol L^{-1} Na$_2$CO$_3$ on solubility. The Sechenov parameters were determined to be 0.170 and 0.373 L mol^{-1}, respectively. Schroder[48] determined the

Table 11. Sechenov salt-effect parameters for dissolving nitrogen in aqueous K$_2$CO$_3$ solutions

T/K	Concentration/ (mol L^{-1})	k_{scc}/ (L mol^{-1})
323.15	0.5	0.272
	1.0	0.263
	2.0	0.240
363.15	0.5	0.477[a]
	1.0	0.456[a]
	2.0	0.250
	4.0	0.209
	6.0	0.143

[a]These values are doubtful. All data from Ref. 48.

effect of K$_2$CO$_3$, with results shown in Table 11. The nitrogen pressure ranged from 10 to 40 MPa. The salt-effect parameter appears to decrease with increased electrolyte concentration.

4.3.c. Group IIA Salts

Group IIA metal salts which have been examined include MgSO$_4$ and CaCl$_2$. The Smith et al.[43] results for MgSO$_4$ (two concentrations, 303.15 K and ca. 1.5–7.0 MPa) lead to k_{scc} values of 0.22 L mol^{-1}, and for CaCl$_2$ (four concentrations, 303.15 K and ca. 1.2–7.3 MPa) k_{scc} values decrease from 0.21 to 0.15 L mol^{-1} with salt concentrations increasing from 0.5 to 5.6 mol L^{-1}. Braun[44] examined the effect of BaCl$_2$ on nitrogen solubility between 278 and 298 K. The values for k_{scc} increased from 0.31 to 0.36 L mol^{-1} as

Table 12. Sechenov salt-effect parameters for dissolving nitrogen at 298.15 K in aqueous acetate solutions

Metal Ion	Concentration/ (mol L^{-1})	k_{scc} (L mol^{-1})
Zn^{2+}	0.15	0.169
Hg^{2+}	0.05	0.083
	0.15	0.113
Cu^{2+}	0.05	0.169
	0.157	0.123
Ni^{2+}	0.051	0.148
	0.15	0.098
Co^{2+}	0.033	0.187
	0.10	0.155
Mn^{2+}	0.05	0.145
	0.15	0.123

[a]Ref. [49].

temperature increased. However, this contradicts the generalization that the salt-effect parameter decreases with increasing temperature.

4.3.d. Other Salts

Brasted and Hirayama[49] measured the effect of several transition metal acetates on the solubility of nitrogen in a mixed solution of 1.0 mol L^{-1} acetic acid and 0.50 mol L^{-1} sodium acetate in water. Unfortunately, they did not measure the solubility of nitrogen in the mixed solution in the absence of transition metal acetates. Consequently, the measured salt-effect parameters listed in Table 12 are for total electrolyte molarity, C_2, which includes the transition metal acetates.

4.4. Solubility of Nitrogen in Organic Solvents Plus Water (0.101 325 MPa)

The solubility of nitrogen in organic solvents plus water has been studied for nine systems. All but two systems were studied at only one laboratory. In ethanol + water mixtures and 1,2,3-propanediol + water mixtures, three groups measured the nitrogen solubilities but at different temperatures or compositions. Thus the comparison of results from different laboratories is difficult and all of the data are classed as tentative.

The mole fraction solubilities (at 0.101 325 MPa partial pressure of nitrogen) in alcohol/water mixtures were fitted by

$$x_1 = A_0 + A_1 x_{ROH} + A_2 x_{ROH}^2 + A_3 x_{ROH}^3, \tag{16}$$

in the composition range between 0.1 to 1 in mole fraction of an alcohol x_{ROH}. The smoothed values of the mole fraction solubility, the coefficients of Eq. (16), and the standard deviation in x_1 are listed in Table 13. The original solubilities in the water-rich region are listed in Table 14. In the alcohol/water mixtures, the solubility shows a maximum in between 0 to 0.1 in x_{ROH}, and then increases after passing through a minimum as the content of the alcohol increases.

4.4.a. Nitrogen Solubilities in Methanol/Water Mixtures

Only Tokunaga[50] measured nitrogen solubilities in methanol/water mixtures at 293.15 and 313.15 K, and

Table 13. Mole fraction solubilities of nitrogen in alcohol/water mixtures at 0.101325 MPa partial pressure of nitrogen, $10^4 x_1$

Mole fraction of alcohols	Methanol/Water		Ethanol/Water		1-Propanol/Water		2-Propanol/Water	
	293.15 K	313.15 K	293.15 K	313.15 K	293.15 K	313.15 K	293.15 K	313.15 K
0.1	0.172	0.136	0.187	0.145	0.234	0.253	0.169	0.168
0.2	0.179	0.190	0.301	0.270	0.461	0.551	0.413	0.434
0.3	0.239	0.277	0.482	0.450	0.729	0.875	0.708	0.752
0.4	0.355	0.403	0.729	0.690	1.039	1.226	1.054	1.123
0.5	0.528	0.574	1.043	0.995	1.391	1.605	1.451	1.546
0.6	0.760	0.796	1.423	1.368	1.784	2.009	1.899	2.021
0.7	1.056	1.075	1.870	1.815	2.218	2.441	2.397	2.548
0.8	1.416	1.417	2.384	2.339	2.694	2.900	2.947	3.128
0.9	1.843	1.828	2.964	2.946	3.211	3.385	3.547	3.760
1.0	2.340	2.315	3.611	3.639	3.770	3.897	4.199	4.443
$10^5 A_0$ [a]	2.1517	1.0841	1.3962	0.7148	0.4819	-0.1771	-0.2364	-0.4657
$10^5 A_1$ [a]	-6.7699	1.6257	1.4111	4.9655	16.4895	25.7445	16.7542	18.8007
$10^5 A_2$ [a]	24.0652	10.2917	33.3031	23.2985	20.7286	13.4015	25.4707	26.0990
$10^5 A_3$ [a]	3.9496	10.1487		7.4102				
$10^4 \alpha$ [b]	0.025	0.041	0.034	0.024	0.026	0.013	0.069	0.051

[a] Coefficients in Eq. (16).

[b] Standard deviation in x_1.

4.4.g. Nitrogen Solubilities in 2-Methylpropanoic Acid/Water Mixtures

Drucker and Moles[53] measured the solubility in the mixture containing 37.5% of 2-methylpropanoic acid at 296.17 and 302.17 K and a pressure range between 0.032 and 0.115 MPa. Their values for the Ostwald coefficient at ca. 0.1013 MPa are 0.0400 at 296.17 K and 0.0386 at 302.17 K.

4.4.h. Nitrogen Solubilities in Acetamide/Water Mixtures

Hüfner[21] measured the solubility in water and a mixture of acetamide and water at an acetamide concentration of 1.0 mol L^{-1} at 293.4 K. His value in pure water is 0.8% lower than the recommended value, and his value in the mixture is 0.014 76 as the Bunsen coefficient.

4.5. Nitrogen in Mixed Solvents (0.101 325 MPa)

The solubility of nitrogen in binary organic solvents has been reported in four papers. Kretschmer et al.[52] studied two systems at three temperatures between 273 and 323 K but at only one composition each. Nitta et al.[56,57] studied five systems covering the whole composition range at one temperature. Finally, Chang and Gokcen[58] studied one system in the whole composition range and in the temperature range 273–303 K. Each system was studied by only one group and the results are considered tentative.

4.5.a. Mixtures of Ethanol Plus 2-Propanone and Ethanol Plus 2,2,4-Trimethylpentane

Kretschmer et al.[52] studied the solubility of nitrogen in these two mixtures at 273.15, 298.15, and 323.15 K, and at only one composition each. Their values are listed in Table 15. The enthalpies and entropies of solution are 2042 J mol^{-1} and -57.5 J mol^{-1} K^{-1} for the mixture of ethanol plus 2-propanone (0.558 mole fraction in ethanol), and 749 J mol^{-1} and -58.0 J mol^{-1} K^{-1} for the mixture of ethanol plus 2,2,4-trimethylpentane (0.739 mole fraction in ethanol), respectively.

Table 15. Mole fraction solubilities of nitrogen in mixtures of ethanol plus 2-propanone and ethanol plus 2,2,4-trimethylpentane at 0.101325 MPa partial pressure of nitrogen, $10^4 x_1$

T/K	2-Propanone[a]	2,2,4-Trimethylpentane[b]
273.15	4.05	6.71
298.15	4.30	6.87
323.15	4.65	7.06

[a]The mixture of ethanol plus 2-propanone where the mole fraction of ethanol is 0.558.

[b]The mixture of ethanol plus 2,2,4-trimethylpentane where the mole fraction of ethanol is 0.739.

Table 16. Mole fraction solubilities of nitrogen in mixtures of acetic acid, ethyl ester (ethyl acetate) plus ethanol; ethane,1,1'-oxybis (diethy ether) plus ethanol; and benzene plus ethanol at 0.101325 MPa partial pressure of nitrogen, $10^4 x_1$

Mole fraction of ethanol[a]	Ethyl acetate[b] (313.15 K)	Diethyl ether[c] (273.15 K)	Benzene[d] (298.15 K)
0.0	8.052	11.97	4.523
0.1000	7.710	11.00	4.454
0.2000	7.236	9.960	4.373
0.3000	6.826	9.099	4.292
0.4000	6.414	8.091	4.153
0.5000	5.963	7.185	4.019
0.6000	5.525	6.398	3.903
0.7000	5.053	5.565	3.824
0.8000	4.566	4.805	3.727
0.9000	4.103	4.114	3.636
1.0	3.614	3.512	3.580

[a]Before absorption of nitrogen.

[b]Mixture of acetic acid, ethyl ester plus ethanol.

[c]Mixture of ethane, 1,1'-oxybis plus ethanol.

[d]Mixture of benzene plus ethanol.

4.5.b. Mixtures of Acetic Acid, Ethyl Ester (Ethyl Acetate) Plus Ethanol, Ethane, 1,1'-Oxybis (Diethyl Ether) Plus Ethanol; and Benzene plus Ethanol

Nitta et al.[57] studied the solubility of nitrogen in these three mixed solvent systems at only one temperature each. Their values are listed in Table 16. The mole fraction solubility of nitrogen is expressed as a function of the mole fraction of ethanol as follows:

$$x_1 = 8.15 \times 10^{-4} - 4.46 \times 10^{-4} x_{ethanol}$$

with an average deviation of 0.7% for the mixture of acetic acid, ethyl ester plus ethanol;

$$x_1 = 11.70 \times 10^{-4} - 8.55 \times 10^{-4} x_{ethanol}$$

with an average deviation of 2.7% for the mixture of ethane, 1,1'-oxybis plus ethanol; and

$$x_1 = 4.54 \times 10^{-4} - 1.00 \times 10^{-4} x_{ethanol}$$

with an average deviation of 0.6% for the mixture of benzene plus ethanol. The deviations from linearity have a qualitative similarity with the excess volumes of the mixed solvents.[52]

4.5.c. Mixtures of 1-Propanol Plus 2,2,4-Trimethylpentane and Cyclohexane Plus 2,2,4-Trimethylpentane

Nitta et al.[56] studied the solubility of nitrogen in these mixtures covering the whole composition range at 298.15 K. Their values are listed in Table 17. The mole fraction solubility of nitrogen as a function of the mole fraction of 2,2,4-trimethylpentane x_{TMP}, in each mixed solvent is expressed as follows: $x_1 = 3.99 \times 10^{-4} + 11.35 \times 10^{-4} x_{TMP}$ with an average deviation of 0.6% for the mixture of 1-propanol plus 2,2,4-trimethylpentane; and

$$x_1 = 7.58 \times 10^{-4} + 7.70 \times 10^{-4} x_{TMP}$$

with an average deviation of 0.1% for the mixture of cyclohexane plus 2,2,4-trimethylpentane.

Table 17. Mole fraction solubilities of nitrogen in mixtures of 1-propanol plus 2,2,4-trimethylpentane; cyclohexane plus 2,2,4-trimethylpentane; and hydrazine plus 1,1-dimethylhydrazine at 0.101325 MPa partial pressure of nitrogen, 10^4 x_1

Mole fraction[a]	1-Propanol[b] (298.15 K)	Cyclohexane[c] (298.15 K)	Hydrazine[d] (288.15 K)
0.0	4.029	7.575	0.0623
0.1000	5.073	8.326	0.160
0.2000	6.188	9.124	0.310
0.3000	7.336	9.90	0.514
0.4000	8.547	10.67	0.774
0.5000	9.727	11.45	1.087
0.6000	10.88	12.19	1.47
0.7000	11.98	12.96	1.90
0.8000	13.04	13.69	2.40
0.9000	14.16	14.51	2.95
1.0	15.30	15.30	3.57

[a]Mole fraction of 2,2,4-trimethylpentane or 1,1-dimethylhydrazine before absorption of nitrogen.

[b]Mixture of 1-propanol plus 2,2,4-trimethylpentane.

[c]Mixture of cyclohexane plus 2,2,4-trimethylpentane.

[d]Mixture of hydrazine plus 1,1-dimethylhydrazine.

4.5.d. Mixtures of Hydrazine Plus 1,1,-Dimethylhydrazine

Chang and Gokcen[58] studied the solubility of nitrogen in the mixtures of hydrazine plus 1,1-dimethylhydrazine covering the whole composition range and the temperature

Table 18. Coefficients[a] for nitrogen solubilities in hydrazine/1,1-dimethylhydrazine mixtures at 0.101325 MPa

Mole fraction of 1,1-dimethylhydrazine	A_0	A_1
0.0	7.850	1188
0.1	7.845	921
0.2	7.850	730
0.3	7.780	604
0.4	7.458	579
0.5	7.136	574
0.6	6.904	554
0.7	6.733	528
0.8	6.622	493
0.9	6.557	453
1.0	6.542	403

[a]$-\ln x_1 = A_0 + A_1/(T/K)$.

range 273–303 K. Their values at 288.15 K are listed in Table 17. The mole fraction solubilities of nitrogen (at 0.101325 MPa partial pressure of nitrogen) at other temperatures can be calculated by $-\ln x_1 = A_0 + A_1/(T/K)$ between 273 to 303 K. The values of A_0 and A_1 are listed in Table 18.

4.6. Nitrogen in Mixed Solvents (above 0.101 325 MPa)

The systems in this section are complicated because the solubility is a function of three variables, i.e., temperature, pressure, and composition of the solvents. The data are not sufficient to allow us to fit the solubility as a function of these three variables together. For acetic acid-cyclohexanone and acetic acid-cyclohexanol-cyclohexanone mixtures, the solubility was fitted as a function of temperature and pressure for a fixed composition of the solvents. The other two systems where the solubility cannot be fitted by a simple equation are the methylcyclohexane-heptane and cyclohexane-oxygen systems. All the data are considered tentative.

4.6.a. Mixtures of Acetic Acid and Cyclohexanone

Khodeeva and Dymova[59] measured the solubility of nitrogen in two mixtures of acetic acid and cyclohexanone. In the mixture of 25 wt. % of cyclohexanone before absorption, their data were fitted to give the following equation in the temperature range 348–473 K and in the pressure range 2.1–8.8 MPa

$$\ln x_1 = -4.1957 - 5.2548/\tau + 0.9893 \ln(P/\text{MPa}), \tag{22}$$

with a standard deviation of 0.059 in $\ln x_1$. In the mixture of 64 wt. % of cyclohexanone before absorption, they measured the solubility at 373.15 and 423.15 K and in the pressure range 2.4–8.3 MPa. The data gave

$$\ln x_1 = -4.6129 - 2.9525/\tau + 0.9926 \ln(P/\text{MPa}) \tag{23}$$

with a standard deviation of 0.035 in $\ln x_1$.

4.6.b. Mixtures of Cyclohexanol, Cyclohexanone, and Acetic Acid

Khodeeva and Dymova[59] measured the solubility of nitrogen in three mixtures of cyclohexanol, cyclohexanone, and acetic acid. In the mixture where the weight fractions before absorption are 0.10, 0.225, and 0.675 for cyclohexanol, cyclohexanone, and acetic acid, respectively, their data at 373.15 and 423.15 K in the pressure range 3.3–11.9 MPa gave

$$\ln x_1 = -4.0791 - 5.3952/\tau + 0.9866 \ln(P/\text{MPa}), \tag{24}$$

with a standard deviation of 0.028 in $\ln x_1$. In the mixture of 0.20, 0.52, 0.28 weight fractions of cyclohexanol, cyclohexanone, and acetic acid, respectively, before absorption, their data at 373.15, 423.15, and 448.15 K in the pressure range 3.1–7.9 MPa gave

$$\ln x_1 = -3.8655 - 5.5169/\tau + 0.9533 \ln(P/\text{MPa}), \tag{25}$$

with a standard deviation of 0.031 in $\ln x_1$. In the mixture of

0.10, 0.585, and 0.315 weight fraction before absorption of cyclohexanol, cyclohexanone, and acetic acid, respectively, their data at 373.15, 423.15, and 448.15 K in the pressure range 2.7–8.6 MPa gave

$$\ln x_1 = -3.7080 - 6.4796/\tau + 1.0176 \ln(P/\text{MPa}) \tag{26}$$

with a standard deviation of 0.040 in $\ln x_1$.

4.6.c. Mixtures of Methylcyclohexane and Heptane

Brunner et al.[60] studied this system in the temperature range 453 to 492 K and in the pressure range 13 to 33 MPa. The number of data points are too small to express them in an analytical form.

4.6.d. Mixtures of Oxygen and Nitrogen in Cyclohexane

Khodeeva[61] measured the solubility of two mixtures of nitrogen and oxygen (0.082 and 0.200 volume fraction of oxygen in the gas phase) in cyclohexane. Total mole fractions of the gases in liquid are available as a function of pressure (4–11 MPa) at 373.15, 403.15, and 433.15 K.

4.7. Nitrogen in Hydrocarbons (0.101 325 MPa)

Nitrogen solubilities have been measured in pure hydrocarbon solvents and mixtures over a wide range of temperature and pressure. With the availability of the SAS program we are using for least-squares (regression) analysis of the data, we have attempted in this section to reduce large quantities of data to a small number of equations. There are, of course, problems of overlapping ranges and also gaps in those ranges, as well as the varying precision not only between papers but as a function of the magnitude of the variables. Still, we felt it worthwhile to attempt a condensation of existing data in this way.

In the next section, we fit the solubility of nitrogen in the n-alkanes at 0.101 325 MPa as a function of the temperature and the number of carbon atoms C. In subsequent sections, we treat saturated and unsaturated hydrocarbons, cyclic hydrocarbons, and aromatic hydrocarbons. In these subsequent sections, the discussion is generally about a single solvent at 0.101 325 MPa. In Sec. 4.8, the pressure dependence is discussed.

4.7.a. n-Alkanes as a Group

The solubility of nitrogen at atmospheric pressure has been measured in the n-alkanes, C_5 to C_{16}, by many different groups. Makranczy et al.[62] measured nitrogen solubilities in the entire series C_5 to C_{16} at 298.15 and 313.15 K. However, there are some discrepancies between their work and that of other groups. The data for smoothing according to the following equation were obtained from Refs. 62–71:

$$\ln x_1 = -15.393 + 11.827/\tau + 4.4606 \ln \tau - 0.015\,587\,C, \tag{27}$$

where C is the number of carbon atoms in the n-alkane. In doing the smoothing individual points which differed by more than two standard deviations from the smoothed data were thrown out. The temperature range for data used for individual solvents is given in parentheses: C_5 (298–313), C_6
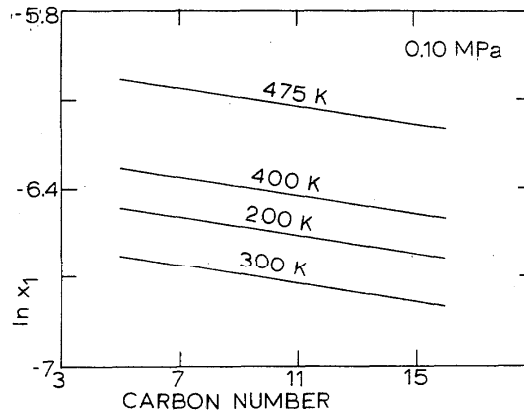
FIG. 2. Mole fraction solubility of nitrogen in the n-alkanes at 0.101 325 MPa as a function of carbon number.

(213–313), C_7 (298–313), C_8 (298–313), C_9 (298–313), C_{10} (283–313), C_{11} through C_{15} (298–313), C_{16} (298–475). The fit to $\ln x_1$ (one standard deviation) was 0.11. Figure 2 shows the smoothed values of x_1 as a function of carbon number at several temperatures. The relatively large standard deviation for nitrogen/n-alkanes taken as a group indicates that these systems are still awaiting a definitive study.

4.7.b. Alkanes Individually

4.7.b.1. n-Pentane

This solvent was only studied by Makranczy et al.,[62] and the mole fraction solubilities they found are 1.45×10^{-3} at 298.15 K and 1.23×10^{-3} at 313.15 K.

4.7.b.2. n-Hexane

The nitrogen/n-hexane system was studied by five groups,[62–66] but Guerry's datum[66] was much too low to be considered. The data from the remaining four papers less the 313.15 K value from Ref. 62 were used in the temperature range 213.15–298.15 K to obtain the following smoothing equation:

$$\ln x_1 = -6.3942 - 0.5539/\tau. \tag{28}$$

The standard deviation in $\ln x_1$ was 0.016 and smoothed values at 10 K intervals are given in Table 19.

Table 19. Nitrogen solubilities in n-hexane at 0.101325 MPa according to Eq. (28)

T/K	$10^3 x_1$	T/K	$10^3 x_1$
213.15	1.29	263.15	1.35
223.15	1.30	273.15	1.36
233.15	1.32	283.15	1.37
243.15	1.33	293.15	1.38
253.15	1.34	298.15	1.39

4.7.b.3. n-Heptane

Nitrogen/n-heptane was studied by four groups[62,66-68] but the work by Thomsen and Gjaldbaek[67] is the most consistent. Their data alone were used to yield

$$\ln x_1 = -6.0478 - 1.6695/\tau, \tag{29}$$

in the range 298–308 K with a standard deviation of 0.0049 in $\ln x_1$.

4.7.b.4. n-Octane

Of the four groups,[62,67-69] studying nitrogen/n-octane the work of Thomsen and Gjaldbaek[67] and Wilcock et al.[69] were judged to be the most reliable. Their data were smoothed in the range 298–308 K to give

$$\ln x_1 = -5.9828 - 1.9483/\tau, \tag{30}$$

with a standard deviation in $\ln x_1$ of 0.0053.

4.7.b.5. 2,2,4-Trimethylpentane

For the nitrogen/2,2,4-trimethylpentane system, we used the results of Kretschmer et al.[52] and Baldwin and Daniel[70] rejecting the Ijams[68] single value. The smoothing equation from 248 to 323 K is

$$\ln x_1 = -6.3069 - 0.5039/\tau, \tag{31}$$

with a standard deviation in $\ln x_1$ of 0.014. Smoothed values are given in Table 20.

4.7.b.6. n-Nonane

For this system, we considered the Thomsen and Gjaldbaek data[67] to be the only reliable work; the average of their results around 298.15 K was $x_1 = 0.001\ 28$. The Makranczy et al.[62] values show too great a temperature dependence when compared with the results of other workers and must be considered as tentative until the system is restudied.

4.7.b.7. n-Decane

We considered Wilcock et al.'s results[69] to be the most reliable here and smoothing their three points in the range 283–313 K gave

$$\ln x_1 = -6.8288 + 0.3404/\tau, \tag{32}$$

with a standard deviation in $\ln x_1$ of 0.000 52. Makranczy et al.'s[62] results were inconsistent with other workers and so was Ijam's.[68]

Table 20. Nitrogen solubilities in 2,2,4-trimethylpentane at 0.101325 MPa according to Eq. (31)

T/K	$10^3 x_1$	T/K	$10^3 x_1$
248.15	1.49	298.15	1.54
258.15	1.50	308.15	1.55
268.15	1.51	318.15	1.56
278.15	1.52	328.15	1.56
288.15	1.53		

Table 21. The solubility of nitrogen in C_{11} to C_{15} n-alkanes at 0.101325 MPa [62]

Solvent	T/K	$10^3 x_1$
Undecane	298.15	1.27
	313.15	1.02
Dodecane	298.15	1.23
	313.15	0.95
Tridecane	298.15	1.24
	313.15	0.97
Tetradecane	298.15	1.24
	313.15	0.95
Pentadecane	298.15	1.26
	313.15	0.93

4.7.b.8. C₁₁ to C₁₅

Only the results of Makranczy et al.,[62] are available for these solvents. We record their results in Table 21 noting that the temperature dependence appears to be too great.

4.7.b.9. n-Hexadecane

Tremper and Prausnitz's work[71] covers a much wider temperature range than that of Makranczy et al.,[62] and we consider the former to be more reliable. Smoothing the former results yields

$$\ln x_1 = -9.8120 - 3.3956/\tau + 1.8304 \ln \tau, \tag{33}$$

with a standard deviation of $\ln x_1$ of 0.0066. Smoothed values for the range 300–475 K are presented in Table 22.

4.7.c. Cyclic Hydrocarbons

Several groups have studied the nitrogen/cyclohexane system and it will be treated individually. Other cyclic hydrocarbon solvents were studied by one group each and they will be treated in one section.

4.7.c.1. Cyclohexane

Seven papers report on the nitrogen/cyclohexane system. We considered the best results to be those reported in four papers which showed good internal consistency as well

Table 22. Nitrogen solubilities in n-hexadecane at 0.101325 MPa. Smoothed results using Eq. (33)

T/K	$10^3 x_1$	T/K	$10^3 x_1$
300	1.27	400	1.62
325	1.35	425	1.72
350	1.43	450	1.83
375	1.52	475	1.94

Table 23. Nitrogen solubilities in cyclohexane at 0.101325 MPa

according to Eq. (34)

T/K	$10^4 x_1$	T/K	$10^4 x_1$
283.15	7.22	313.15	8.22
288.15	7.39	318.15	8.38
293.15	7.56	323.15	8.54
298.15	7.73	328.15	8.70
303.15	7.89	333.15	8.85
308.15	8.06		

as with each other.[72-75] These results were smoothed in the range 283–333 K to yield

$$\ln x_1 = -5.8738 - 3.8518/\tau, \qquad (34)$$

with a standard deviation of 0.010 in $\ln x_1$. Smoothed results are presented in Table 23.

For this system Guerry's two points[66] were much too low. The single points obtained by Gjaldbaek and Hildebrand[63] and Patyi et al.,[65] were in reasonable agreement with the recommended values in Table 23. Wild et al.'s[75] results were obtained via two methods which showed good internal agreement at partial pressures of nitrogen up to 1.9 MPa and over a wide temperature range (300 to 443 K). We used their gas chromatograph data for Eq. (34).

4.7.c.2. Other Cyclic Hydrocarbons

Mole fraction solubilities at 0.101 325 MPa partial pressure of gas for nitrogen solubilities in several cyclic hydrocarbons are given in Table 24.

Table 24. Nitrogen solubilities in several cyclic hydrocarbons

at 0.101325 MPa

Solvent	T/K	$10^4 x_1$
Cyclohexene	293.15	6.10[a]
	298.15	6.22[a]
Methylcyclohexane	284.29	8.49[b]
	298.18	9.46[b]
	313.27	9.88[b]
Cyclooctane	289.04	5.70[c]
	298.26	5.98[c]
	313.52	6.60[c]
cis-1,2-Dimethylcyclohexane	297.97	8.84[d]
	312.97	9.23[d]
trans-1,2-Dimethylcyclohexane	298.25	10.01[d]
	313.01	10.16[d]
70 mol % cis-1,4-Dimethylcyclohexane	298.17	9.97[d]
+ 30 mol % trans-1,4-dimethylcyclohexane	313.15	10.29[d]
59 mol % cis-1,3-Dimethylcyclohexane	298.07	10.05[d]
+ 41 mol % trans-1,3-dimethylcyclohexane	313.01	10.43[d]

[a][66]   [b][76]   [c][77]   [d][78]

Table 25. Nitrogen solubility in 1,1'-bicyclohexyl

at 0.101325 MPa [71]

T/K	$10^4 x_1$	T/K	$10^4 x_1$
300	7.435	400	9.606
325	7.849	425	10.58
350	8.333	450	12.06
375	8.905	475	13.97

In Table 25, we present the solubility data of Tremper and Prausnitz[71] in 1,1'-bicyclohexyl.

4.7.d. Aromatic Hydrocarbons

4.7.d.1. Benzene

Six groups[51,63,65,79-81] report on the solubility of nitrogen in benzene. The two points reported by Just[51] were significantly lower and Patyi et al.'s[65] single point significantly higher than the values obtained by smoothing the other four papers' results. Yen and McKetta's results at 301 K were low.[80] The smoothing equation is

$$\ln x_1 = -6.054\,45 - 4.956\,73/\tau, \qquad (35)$$

with a standard deviation in $\ln x_1$ of 0.0090. Smoothed values are given in Table 26.

4.7.d.2. Toluene

Just[51] and Field et al.,[76] both studied nitrogen/toluene and their data were combined to give

$$\ln x_1 = -6.275\,76 - 3.716\,75/\tau, \qquad (36)$$

with a standard deviation in $\ln x_1$ of 0.030. Smoothed values are given in Table 27 for the range 283–313 K.

4.8. Nitrogen in Hydrocarbons (above 0.101 325 MPa)

In the previous section, we discussed nitrogen solubilities in saturated and unsaturated hydrocarbon solvents at pressures around atmospheric. In this section, we discuss the higher pressure results. There is considerable literature on nitrogen solubilities in mixed solvents (i.e., ternary systems). We will not cover these systems in this review, but they are

Table 26. The solubility of nitrogen in benzene at 0.101325 MPa

according to Eq. (35)

T/K	$10^4 x_1$	T/K	$10^4 x_1$
278.15	3.95	308.15	4.70
283.15	4.08	313.15	4.82
288.15	4.20	318.15	4.94
293.15	4.33	323.15	5.06
298.15	4.45	328.15	5.18
303.15	4.58	333.15	5.30

Table 27. The solubility of nitrogen in toluene at 0.101325 MPa according to Eq. (36)

T/K	$10^4 x_1$	T/K	$10^4 x_1$
283.15	5.06	303.15	5.52
288.15	5.18	308.15	5.63
293.15	5.29	313.15	5.74
298.15	5.41		

discussed in Ref. 1. Also, inevitably, the overlap between a "solubility" and "vapor-liquid equilibrium" becomes much evident at higher pressures. We consider the data reported on herein as "solubilities" although there is much leeway for debate on some systems under some conditions. Pressures are total pressures.

In what follows, systems are generally discussed individually. For most of them we have successfully fitted the data using SAS[19] as a function of both temperature and pres-

Table 28. Nitrogen solubilities at 0.101325 MPa in three aromatic solvents

Solvent	T/K	$10^4 x_1$
Xylene[a]	293.15	6.03[b]
	298.15	6.12[b]
1-Methyl naphthalene	300	3.367[c]
	325	3.664[c]
	350	4.031[c]
	375	4.500[c]
	400	5.131[c]
	425	6.042[c]
	450	7.474[c]
	475	9.025[c]
1,1'-Methylenebisbenzene	300	3.405[c]
(diphenylmethane)	325	3.891[c]
	350	4.340[c]
	375	4.805[c]
	400	5.291[c]
	425	5.824[c]
	450	6.439[c]
	475	7.037[c]

[a]See text.   [b][51]   [c][71]
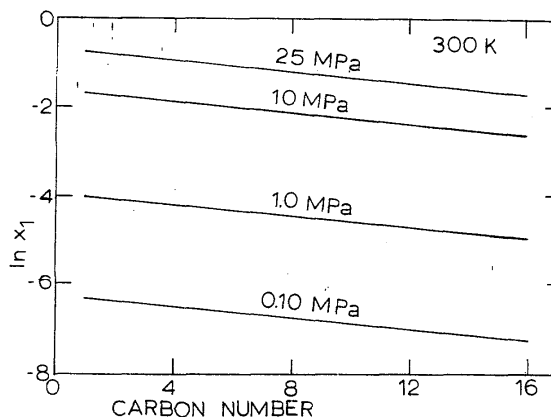
FIG. 3. Mole fraction solubility of nitrogen in the n-alkanes at 300 K as a function of carbon number.

sure. Data at atmospheric pressure have been incorporated into these fits unless otherwise specified. We have also attempted to fit the data as a function of temperature, pressure, and carbon number for the n-alkanes.

4.8.a. The n-Alkanes as a Group

Since the SAS program permits it, we attempted to fit grouped nitrogen solubilities as a function of temperature, pressure and carbon number. The results of this treatment gave the following equation for C_1 to C_{16} from 0.101 MPa to 75 MPa and 273 to 500 K:

$$\ln x_1 = -12.882 + 12.268/\tau + 4.4131 \ln \tau$$
$$+ 1.0098 \ln(P/\mathrm{MPa}) - 0.062\,824\,C, \qquad (37)$$

with a standard deviation of 0.44 in $\ln x_1$. The precision is necessarily poor using such an amount of data from so many sources and over such wide ranges of conditions. Nevertheless, Eq. (37) should prove to be useful for semiquantitative purposes. For illustrative purposes, we give Figs. 3, 4, and 5 which show $\ln x_1$ versus C for several isotherm/isobar combinations. In Tables 29, 30, and 31, we present smoothed
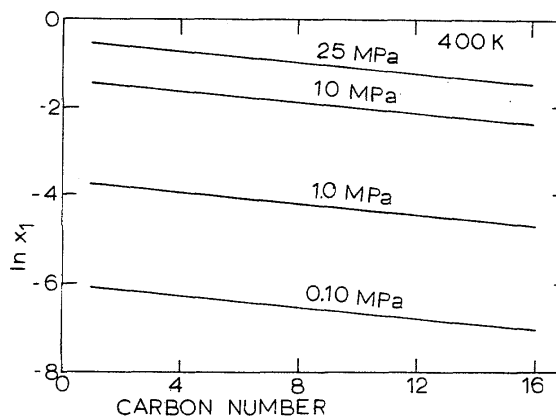
FIG. 4. Mole fraction solubility of nitrogen in the n-alkanes at 400 K as a function of carbon number.
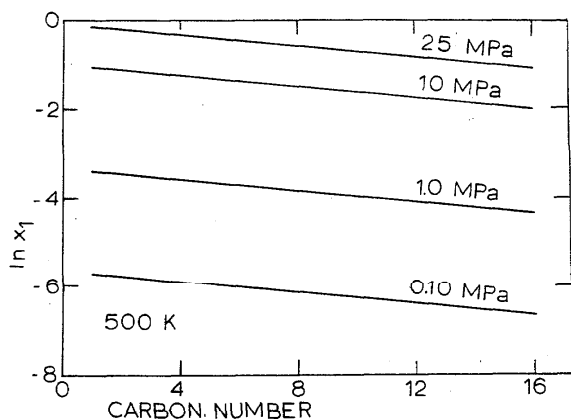
FIG. 5. Mole fraction solubility of nitrogen in the n-alkanes at 500 K as a function of carbon number.

Table 30. Smoothed mole fraction solubilities of nitrogen in the n-alkanes (Eq. (37)) at 400 K

c [a]	0.101 MPa	1.0 MPa	10.0 MPa	25.0 MPa	50.0 MPa	75.0 MPa
1	0.00231	0.0233	0.238	0.601	-[b]	-
2	0.00217	0.0219	0.224	0.564	-	-
3	0.00203	0.0205	0.210	0.530	-	-
4	0.00191	0.0193	0.197	0.498	-	-
5	0.00179	0.0181	0.185	0.467	0.941	-
6	0.00169	0.0170	0.174	0.439	0.884	-
7	0.00158	0.0160	0.163	0.412	0.830	-
8	0.00149	0.0150	0.153	0.387	0.779	-
9	0.00140	0.0141	0.144	0.363	0.732	-
10	0.00131	0.0132	0.135	0.341	0.687	-
11	0.00123	0.0124	0.127	0.321	0.645	0.972
12	0.00116	0.0117	0.119	0.301	0.606	0.913
13	0.00109	0.0110	0.112	0.283	0.569	0.857
14	0.00102	0.0103	0.105	0.265	0.535	0.805
15	0.00096	0.0097	0.099	0.249	0.502	0.756
16	0.00090	0.0091	0.093	0.234	0.471	0.710

[a] Number of carbon atoms in n-alkane.

[b] Dash indicates mole fraction greater than 1.0.

data according to Eq. (37) at 300, 400, and 500 K, respectively. At the higher temperatures and pressures, the smoothing function predicts mole fraction solubilities greater than one. This is, of course, an artifact of the fitting process. Caution should be employed when using these tables.

4.8.b. Methane

This system has been studied intensively. We found the results reported in seven papers[82-88] to be consistent with each other and have used their data to obtain the following equation:

$$\ln x_1 = 0.345\,72 - 10.4175 \ln \tau + 0.288\,87(P/\mathrm{MPa})$$
$$+ 1.518\,47 \ln(P/\mathrm{MPa}), \tag{38}$$

valid over the range 0.02 to 5.0 MPa and 91 and 187 K. The standard deviation in ln x_1 was 0.17. Smoothed data are presented in Table 32.

4.8.c. Ethene

The nitrogen/ethene system was studied by three groups[89-91] in the combined ranges of 120 to 260 K and 0.5 to

Table 29. Smoothed mole fraction solubilities of nitrogen in the n-alkanes (Eq. (37)) at 300 K

c [a]	0.101 MPa	1.0 MPa	10.0 MPa	25.0 MPa	50.0 MPa	75.0 MPa
1	1.80x10⁻³	0.0182	0.186	0.469	0.945	-[b]
2	1.69	0.0171	0.175	0.441	0.887	-
3	1.59	0.0160	0.164	0.414	0.833	-
4	1.49	0.0151	0.154	0.389	0.782	-
5	1.40	0.0141	0.145	0.365	0.734	-
6	1.32	0.0133	0.136	0.343	0.690	-
7	1.24	0.0125	0.128	0.322	0.648	0.976
8	1.16	0.0117	0.120	0.302	0.609	0.917
9	1.09	0.0110	0.113	0.284	0.572	0.861
10	1.02	0.0103	0.106	0.267	0.537	0.808
11	0.96	0.0097	0.099	0.250	0.504	0.759
12	0.90	0.0091	0.093	0.235	0.473	0.713
13	0.85	0.0086	0.088	0.221	0.445	0.669
14	0.80	0.0080	0.082	0.207	0.417	0.629
15	0.75	0.0075	0.077	0.195	0.392	0.590
16	0.70	0.0071	0.072	0.183	0.368	0.554

[a] Number of carbons in n-alkane.

[b] Dash indicates mole fraction greater than 1.0.

Table 31. Smoothed mole fraction solubilities of nitrogen in the n-alkanes (Eq. (37)) at 500 K

c [a]	0.101 MPa	1.0 MPa	10.0 MPa	25.0 MPa	50.0 MPa	75.0 MPa
1	0.00334	0.0337	0.345	0.871	-[b]	-
2	0.00314	0.0317	0.324	0.818	-	-
3	0.00295	0.0298	0.304	0.768	-	-
4	0.00277	0.0280	0.286	0.721	-	-
5	0.00260	0.0263	0.269	0.677	-	-
6	0.00244	0.0247	0.252	0.636	-	-
7	0.00229	0.0232	0.237	0.597	-	-
8	0.00215	0.0217	0.222	0.561	-	-
9	0.00202	0.0204	0.209	0.527	-	-
10	0.00190	0.0192	0.196	0.495	0.996	-
11	0.00178	0.0180	0.184	0.465	0.936	-
12	0.00168	0.0169	0.173	0.436	0.879	-
13	0.00157	0.0159	0.162	0.410	0.825	-
14	0.00148	0.0149	0.153	0.385	0.775	-
15	0.00139	0.0140	0.143	0.361	0.728	-
16	0.00130	0.0132	0.135	0.339	0.683	-

[a] Number of carbons in n-alkane.

[b] Dash indicates mole fraction greater than 1.0.

Table 32. Mole fraction nitrogen solubilities in liquid methane

according to Eq. (38)

T/K	0.101 MPa	1.0 MPa	2.0 MPa	3.0 MPa	4.0 MPa	5.0 MPa
90	0.135	-[a]	-	-	-	-
100	0.0450	-	-	-	-	-
120	6.73×10^{-3}	0.282	-	-	-	-
140	1.35×10^{-3}	0.0567	0.217	0.535	-	-
160	3.36×10^{-4}	0.0141	0.0529	0.133	0.275	0.516
180	9.86×10^{-5}	4.13×10^{-3}	0.0158	0.0391	0.0807	0.151
200	3.29×10^{-5}	1.38×10^{-3}	5.27×10^{-3}	0.0130	0.0269	0.0504
210	1.98×10^{-5}	8.30×10^{-4}	3.17×10^{-3}	7.84×10^{-3}	0.0162	0.0303

[a]Dash indicates calculated value greater than 1.0.

Table 34. Mole fraction nitrogen solubilities in liquid ethane

according to Eq. (40)

T/K	0.101 MPa	1.0 MPa	5.0 MPa	10.0 MPa	13.5 MPa
100	0.82×10^{-5}	-[a]	-	-	-
125	1.79	1.48×10^{-4}	0.85×10^{-3}	2.32×10^{-3}	3.97×10^{-3}
150	3.02	2.49	1.43	3.91	6.70
175	4.39	3.62	2.07	5.67	9.73
200	5.81	4.79	2.74	7.50	12.86
225	7.22	5.95	3.41	9.32	15.99
250	8.59	7.08	4.06	11.09	19.03
275	9.90	8.17	4.68	12.79	21.94
300	11.15	9.19	5.26	14.40	24.70

[a]Vapor pressure of nitrogen less than indicated pressure at dash.

11 MPa. Their data were combined to give

$$\ln x_1 = -5.6040 + 3.4541/\tau$$
$$+ 0.065\,000(P/\text{MPa}) + 0.983\,64\ln(P/\text{MPa}),$$
$$(39)$$

with a standard deviation of 0.033 in $\ln x_1$. Smoothed data are given in Table 33.

4.8.d. Ethane

The data from six papers[84,89,90,92-94] were used for smoothing for the nitrogen/ethane system in the ranges 122–301 K and 0.35–13.5 MPa. The smoothing equation is

$$\ln x_1 = -5.7645 - 3.9149/\tau$$
$$+ 0.077\,743(P/\text{MPa}) + 0.891\,04\ln(P/\text{MPa})$$
$$(40)$$

with a standard deviation of 0.18 in $\ln x_1$. Smoothed data are given in Table 34.

4.8.e. Propene

Two groups studied the nitrogen/propene system but under conditions that are quite divergent. We present smoothing equations for each author's work separately. Blagoi and Orobinskii[95] studied this system from 79 to 91 K and

from 0.03 to 0.25 MPa. Their data were smoothed to give

$$\ln x_1 = -7.9433 + 5.1633/\tau + 1.0911\ln(P/\text{MPa}),$$
$$(41)$$

with a standard deviation of 0.13 in $\ln x_1$.

Grauso et al.[90] studied this system in the ranges 260–290 K and 1.7–19.1 MPa. Smoothing their data gave

$$\ln x_1 = -5.1748 + 1.4799/\tau + 1.2670\ln(P/\text{MPa}),$$
$$(42)$$

with a standard deviation of 0.11 in $\ln x_1$.

Interestingly, combining the two sets of data in the ranges 79–290 K and 0.03–19.1 MPa gave

$$\ln x_1 = -5.7678 + 3.5032/\tau + 1.1920\ln(P/\text{MPa})$$
$$(43)$$

with a standard deviation of 0.15 in $\ln x_1$. Smoothed data are presented in Table 35.

4.8.f. Propane

For nitrogen/propane, the results from five papers[83,89,90,96,97] in the combined ranges 92–353 K and 0.1–

Table 33. Mole fraction nitrogen solubilities in liquid ethene

according to Eq. (39)

T/K	0.101 MPa	1.0 MPa	5.0 MPa	10.0 MPa
120	6.94×10^{-3}	6.99×10^{-2}	-[a]	-[a]
140	4.60	4.63	0.293	0.801
160	3.38	3.40	0.215	0.588
180	2.66	2.68	0.169	0.463
200	2.19	2.21	0.140	0.382
220	1.87	1.89	0.119	0.327
240	1.64	1.66	0.105	0.287
260	1.47	1.48	0.094	0.257

[a]Calculated value greater than 1.0 or vapor pressure of nitrogen less than indicated pressure at this temperature.

Table 35. Mole fraction nitrogen solubilities in liquid propene

according to Eq. (43)

T/K	0.101 MPa	1.0 MPa	5.0 MPa	10.0 MPa	15.0 MPa	20.0 MPa
100	6.78×10^{-3}	-[a]	-	-	-	-
125	3.37	0.0515	-	-	-	-
150	2.11	0.0323	0.220	0.503	0.815	-
175	1.51	0.0231	0.158	0.360	0.584	0.823
200	1.18	0.0180	0.123	0.280	0.455	0.641
225	0.97	0.0148	0.101	0.231	0.374	0.527
250	0.83	0.0127	0.086	0.197	0.320	0.451
275	0.73	0.0112	0.076	0.174	0.282	0.397
300	0.66	0.0101	0.068	0.156	0.254	0.357

[a]Dash indicates calculated mole fraction greater than 1.0 or vapor pressure of nitrogen less than indicated pressure.

Table 36. Mole fraction nitrogen solubilities in liquid propane according to Eq. (44)

T/K	0.101 MPa	1.0 MPa	5.0 MPa	10.0 MPa	15.0 MPa	20.0 MPa
100	8.69×10^{-3}	$-^a$	-	-	-	-
125	4.78	3.69×10^{-2}	-	-	-	-
150	3.60	2.67	0.122	0.252	0.406	0.589
175	2.90	2.24	0.102	0.212	0.340	0.494
200	2.65	2.04	0.093	0.193	0.311	0.451
225	2.55	1.97	0.090	0.186	0.299	0.434
250	2.53	1.95	0.089	0.185	0.297	0.431
275	2.57	1.99	0.090	0.188	0.302	0.438
300	2.65	2.05	0.093	0.193	0.311	0.451
325	2.76	2.13	0.097	0.201	0.324	0.470
350	2.90	2.23	0.102	0.211	0.340	0.493

^{a}Dash indicates mole fraction greater than 1.0 or vapor pressure of nitrogen less than indicated pressure.

21.9 MPa were processed as a group to give

$$\ln x_1 = -8.2573 + 5.5313/\tau$$
$$+ 2.2768 \ln \tau + 0.023\,530(P/\text{MPa})$$
$$+ 0.883\,34 \ln(P/\text{MPa}), \qquad (44)$$

with a standard deviation of 0.084 in $\ln x_1$. Smoothed results are presented in Table 36.

4.8.g. n-Butane

Four groups studied the nitrogen/n-butane system,[98-101] but the results of Frolich et al.,[98] are in marked disagreement with the other three more recent sets of data. Thus the data from Refs. 99–101 were used to obtain

$$\ln x_1 = -9.3627 + 6.1155/\tau$$
$$+ 2.9140 \ln \tau + 0.968\,59 \ln(P/\text{MPa}), \qquad (45)$$

with a standard deviation of 0.21 in $\ln x_1$. Smoothed values over a combined range of 153–422 K and 0.5–27.7 MPa (original results) are given in Table 37.

Table 37. Mole fraction nitrogen solubilities in liquid n-butane according to Eq. (45)

T /K	0.101 MPa	1.0 MPa	5.0 MPa	10.0 MPa	20.0 MPa	30.0 MPa
150	1.80×10^{-3}	0.0165	0.078	0.154	0.300	0.445
175	1.57	0.0144	0.069	0.134	0.263	0.389
200	1.50	0.0138	0.065	0.128	0.251	0.371
225	1.50	0.0138	0.066	0.129	0.252	0.373
250	1.56	0.0143	0.068	0.133	0.261	0.386
275	1.65	0.0151	0.072	0.141	0.275	0.408
300	1.76	0.0162	0.077	0.151	0.295	0.437
325	1.90	0.0175	0.083	0.163	0.318	0.471
350	2.07	0.0190	0.090	0.176	0.345	0.511
375	2.25	0.0206	0.098	0.192	0.376	0.557
400	2.45	0.0225	0.107	0.209	0.410	0.607
425	2.67	0.0245	0.117	0.228	0.447	0.662

4.8.h. 2-Methylpropane (Isobutane)

One group reported on this system in two papers.[102,103] The combined data covered the ranges 255–394 K and 0.2–20.8 MPa. The following equation smooths the data:

$$\ln x_1 = -4.6327 + 0.391\,03 \ln \tau$$
$$+ 1.1000 \ln(P/\text{MPa}), \qquad (46)$$

with a standard deviation in $\ln x_1$ of 0.14.

4.8.i. n-Pentane

Kalra et al.'s[104] data on the nitrogen/n-pentane system were smoothed to give the following equation for 277–378 K and 0.1–20.8 MPa:

$$\ln x_1 = -5.1561 + 0.74687 \ln \tau$$
$$+ 1.0441 \ln(P/\text{MPa}). \qquad (47)$$

The standard deviation in $\ln x_1$ was 0.11.

4.8.j. 2-Methylbutane

Krishnan et al.[105] measured the solubility of nitrogen in 2-methylbutane from 278 to 377 K and 0.33 to 20.8 MPa. Smoothing their data yielded

$$\ln x_1 = -5.0682 + 0.61932 \ln \tau$$
$$+ 1.0902 \ln(P/\text{MPa}), \qquad (48)$$

with a standard deviation of 0.088 in $\ln x_1$.

4.8.k. n-Hexane

Poston and McKetta[106] and Baranovich and Smirnova[107] both studied this system. The former in the ranges 311–444 K and 1.7–34.5 MPa and the latter 233–293 K and 0.2–0.7 MPa. Both sets of data were combined to yield

$$\ln x_1 = -12.4959 + 10.7058/\tau$$
$$+ 4.0535 \ln \tau - 9.6932 \times 10^{-3}(P/\text{MPa})$$
$$+ 1.0623 \ln(P/\text{MPa}), \qquad (49)$$

with a standard deviation of 0.082 in $\ln x_1$.

4.8.l. n-Heptane

This system was studied by five groups[60,99,108-110] in the combined ranges of 298–497 K and 0.5–69.1 MPa. Their data were smoothed to give

$$\ln x_1 = -6.9254 + 1.6157 \ln \tau$$
$$- 0.016\,015(P/\text{MPa}) + 1.3059 \ln(P/\text{MPa}), \qquad (50)$$

with a standard deviation of 0.10 in $\ln x_1$. Combining with the 0.101 325 MPa data gave

$$\ln x_1 = -6.0895 + 1.4280 \ln \tau + 0.9759 \ln(P/\text{MPa}), \qquad (51)$$

with a standard deviation of 0.16 in $\ln x_1$. Smoothed data based on this latter equation are presented in Table 38.

4.8.m. n-Octane

Baranovich and Smirnova[107] (233–293 K and 0.2–0.7 MPa) and Graham and Weale[111] (323–373 K and 10.1–30.4

TABLE 30. Mole fraction nitrogen solubilities in liquid n-heptane according to Eq. (51)

T /K	0.101 MPa	1.0 MPa	10.0 MPa	30.0 MPa	50.0 MPa	70.0 MPa
300	0.00117	0.0109	0.103	0.301	0.495	0.687
325	0.00131	0.0122	0.115	0.337	0.555	0.771
350	0.00145	0.0136	0.128	0.375	0.617	0.857
375	0.00160	0.0150	0.142	0.414	0.681	0.945
400	0.00176	0.0164	0.155	0.453	0.747	-
425	0.00192	0.0179	0.169	0.494	0.814	-
450	0.00208	0.0194	0.184	0.537	0.883	-
475	0.00225	0.0210	0.198	0.580	0.954	-
500	0.00242	0.0226	0.213	0.624	-[a]	-

[a]Calculated mole fraction at dashes greater than 1.0.

MPa) studied this system in nonoverlapping ranges. Their data were combined to give

$$\ln x_1 = -13.5566 + 12.4377/\tau$$
$$+ 4.3390 \ln \tau - 0.022\ 130(P/\text{MPa})$$
$$+ 1.1686 \ln(P/\text{MPa}), \tag{52}$$

with a standard deviation of 0.051 in $\ln x_1$. When combined with data at 0.101 325 MPa the smoothing equation was

$$\ln x_1 = -5.8723 + 1.1633 \ln \tau$$
$$+ 0.969\ 99 \ln(P/\text{MPa}), \tag{53}$$

with a standard deviation of 0.14 in $\ln x_1$.

4.8.n. 2,2,4-Trimethylpentane

Graham and Weale[111] and Peter and Ficke[109] both studied this system with combined ranges of 323–453 K and 0.1–61.8 MPa. Both sets of data were combined to yield

$$\ln x_1 = -4.980\ 95 + 0.668\ 40 \ln \tau$$
$$- 0.005\ 179\ 4(P/\text{MPa}) + 0.990\ 00(P/\text{MPa}), \tag{54}$$

with a standard deviation of 0.054 in $\ln x_1$. When combined with 0.101 325 MPa data the equation is

$$\ln x_1 = -4.9012 + 0.62131 \ln \tau$$
$$- 0.004\ 689\ 6(P/\text{MPa}) + 0.980\ 22 \ln(P/\text{MPa}). \tag{55}$$

4.8.o. n-Decane

Azarnoosh and McKetta[112] determined the solubility of nitrogen in n-decane from 298 to 411 K and 2.8 to 34.5 MPa. Their extensive data were smoothed to give

$$\ln x_1 = -4.6812 + 0.366\ 79 \ln \tau$$
$$- 0.012\ 868(P/\text{MPa}) + 1.0343 \ln(P/\text{MPa}), \tag{56}$$

with a standard deviation of 0.020 in $\ln x_1$. With 0.101 325

MPa data this is

$$\ln x_1 = -4.7005 + 0.3632 \ln \tau$$
$$- 0.013857(P/\text{MPa}) + 1.0496 \ln(P/\text{MPa}), \tag{57}$$

and the same standard deviation.

4.8.p. n-Dodecane

Rupprecht and Faeth[113] measured this system, 297–373 K and 0.10–10.3 MPa, and their eight points were smoothed with 0.101 325 MPa data to give

$$\ln x_1 = -155.366 + 226.673/\tau$$
$$+ 68.610 \ln \tau + 1.0031 \ln(P/\text{MPa}), \tag{58}$$

with a standard deviation of 0.024 in $\ln x_1$.

4.8.q. n-Hexadecane

This system was measured by Sultanov et al.,[114] 323–523 K and 4.9–58.8 MPa. Smoothing their data yielded

$$\ln x_1 = -5.1480 + 1.1843 \ln \tau + 0.713\ 27 \ln(P/\text{MPa}), \tag{59}$$

with a standard deviation of 0.14 in $\ln x_1$. With 0.101 325 MPa data this is

$$\ln x_1 = -5.7064 + 1.2002 \ln \tau$$
$$- 0.015\ 411(P/\text{MPa}) + 1.0262 \ln(P/\text{MPa}), \tag{60}$$

with 0.13 as the standard deviation in $\ln x_1$.

4.8.r. Cyclohexane

Khodeeva[61] (373–433 K, 5–10 MPa) studied this system and his data were smoothed to yield

$$\ln x_1 = -6.2681 + 1.1157 \ln \tau + 1.0543 \ln(P/\text{MPa}), \tag{61}$$

with a standard deviation of 0.021 in $\ln x_1$. Wild et al.[75] (300–443 K, 0.1–1.9 MPa) also studied this system and calculated average Henry's law constants over wide pressure ranges. Their data were not suitable for processing with the high pressure data. However, processing the Khodeeva data with the 0.101 325 MPa data (including Ref. 75) gave

$$\ln x_1 = -3.4329 - 4.4893/\tau + 0.973\ 29 \ln(P/\text{MPa}), \tag{62}$$

with 0.025 standard deviation in $\ln x_1$.

4.8.s. Methylcyclohexane

This system was reported on twice[60,109] by the same group and their data in the combined ranges 376–492 K and 2.0–68.7 MPa were smoothed to give

$$\ln x_1 = -7.0135 + 1.6966 \ln \tau$$
$$- 0.005\ 861(P/\text{MPa}) + 1.0843 \ln(P/\text{MPa}), \tag{63}$$

with a standard deviation of 0.071 in $\ln x_1$. With 0.101 325

MPa data this is

$$\ln x_1 = -22.0484 + 26.1140/\tau$$

$$+ 7.8950 \ln \tau - 0.003\ 635\ 2(P/\text{MPa})$$

$$+ 1.0264 \ln(P/\text{MPa}), \tag{64}$$

with a standard deviation of 0.076 in $\ln x_1$.

4.8.t. Benzene

The nitrogen/benzene system was studied by Miller and Dodge[115] (303–423 K, 6.2–30.7 MPa) and Krichevskii and Efremova[116] (288 K, 2.7–78.5 MPa). Both sets of data were combined to give

$$\ln x_1 = -7.4974 + 1.9422 \ln \tau$$

$$- 0.006\ 175\ 0(P/\text{MPa}) + 0.974\ 81 \ln(P/\text{MPa}), \tag{65}$$

with a standard deviation of 0.025 in $\ln x_1$. With 0.101 325 MPa data this is

$$\ln x_1 = -7.5081 + 1.9052 \ln \tau$$

$$- 0.007\ 291\ 9(P/\text{MPa}) + 1.0024 \ln(P/\text{MPa}), \tag{66}$$

with a standard deviation of 0.025 in $\ln x_1$. These smoothed data are presented in Table 39.

4.8.u. Toluene

The nitrogen/toluene system was studied by Tsiklis et al.[117] in the ranges 478–548 K and 1.5–40.5 MPa. Their data were smoothed to give

$$\ln x_1 = -8.1050 + 1.6826 \ln \tau$$

$$- 0.016\ 738(P/\text{MPa}) + 1.4311 \ln(P/\text{MPa}), \tag{67}$$

with a standard deviation of 0.085 in $\ln x_1$. Adding the 0.101 325 MPa data gave

$$\ln x_1 = -42.3551 + 64.6141/\tau$$

$$+ 14.9643 \ln \tau - 0.015\ 769(P/\text{MPa})$$

$$+ 1.4053 \ln(P/\text{MPa}), \tag{68}$$

Table 39. Mole fraction nitrogen solubilities in benzene

T/K	0.101 MPa	1.0 MPa	10.0 MPa	25.0 MPa	50.0 MPa	75.0 MPa
280	3.93×10^{-4}	0.00387	0.0365	0.082	0.137	0.171
290	4.20	0.00414	0.0390	0.088	0.146	0.183
300	4.48	0.00442	0.0416	0.093	0.156	0.195
310	4.77	0.00470	0.0443	0.099	0.166	0.208
320	5.07	0.00500	0.0470	0.106	0.176	0.221
330	5.37	0.00530	0.0499	0.112	0.187	0.234
340	5.69	0.00561	0.0528	0.119	0.198	0.248
350	6.01	0.00592	0.0558	0.125	0.209	0.262
360	6.34	0.00625	0.0589	0.132	0.221	0.276
370	6.68	0.00659	0.0620	0.139	0.233	0.291
380	7.03	0.00693	0.0653	0.147	0.245	0.306
390	7.39	0.00728	0.0686	0.154	0.257	0.322
400	7.75	0.00764	0.0620	0.162	0.270	0.338

Table 40. Mole fraction nitrogen solubilities in toluene

T/K	0.101 MPa	1.0 MPa	10.0 MPa	20.0 MPa	30.0 MPa	40.0 MPa
275	9.69×10^{-4}	0.0238	0.526	-[a]	-	-
300	5.02	0.0124	0.273	0.617	0.932	-
325	3.18	0.0078	0.172	0.390	0.589	0.754
350	2.33	0.0057	0.126	0.286	0.431	0.552
375	1.91	0.0047	0.104	0.234	0.354	0.453
400	1.71	0.0042	0.093	0.210	0.317	0.405
425	1.64	0.0040	0.089	0.201	0.303	0.388
450	1.65	0.0041	0.090	0.203	0.307	0.392
475	1.74	0.0043	0.095	0.214	0.323	0.414
500	1.90	0.0047	0.103	0.234	0.353	0.452
525	2.13	0.0053	0.116	0.262	0.396	0.507
550	2.45	0.0060	0.133	0.301	0.454	0.581

[a]Dash indicates calculated value greater than 1.0.

with 0.062 standard deviation in $\ln x_1$. The smoothed data are presented in Table 40.

4.9. Nitrogen in Organic Compounds Containing Oxygen (0.101 325 MPa)

The solubility of nitrogen in five alcohols was studied in the temperature range 213–323 K by two or more groups each. The solubility in 2-propanone (acetone); acetic acid, methyl ester (methyl acetate); and 1,1'-oxybisethane (diethylether) was studied in the temperature range 194–314 K by one to three groups each. Other solvents were studied in narrower temperature ranges. Alcohols will be discussed as

Table 41. Mole fraction solubilities of nitrogen in five alcohols at 0.101325 MPa partial pressure of nitrogen, $10^4\ x_1$

T/K	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol
213.15	2.84	3.69	4.25	4.59	4.54
223.15	2.78	3.62	4.14	4.60	4.55
233.15	2.74	3.57	4.07	4.61	4.56
243.15	2.72	3.54	4.02	4.62	4.57
253.15	2.70	3.52	3.99	4.63	4.58
263.15	2.70	3.52	3.98	4.64	4.59
273.15	2.70	3.52	3.99	4.74	4.59
283.15	2.71	3.54	4.01	4.75	4.60
293.15	2.72	3.56	4.04	4.66	4.61
298.15	2.73	3.57	4.06	4.66	4.61
303.15	2.74	3.59		4.66	4.61
313.15	2.77	3.62		4.67	4.62
323.15	2.80	3.67		4.67	4.62
A_0^a	-12.2191	-12.0072	-12.8583	-7.63455	-7.64505
A_1^a	5.3738	5.4184	6.7433	-0.110188	-0.111660
A_2^a	2.0242	2.0625	2.5506		
σ^b	0.006	0.016	0.025	0.026	0.026

[a]Coefficients in Eq. (5).

[b]Standard deviation in $\ln x_1$.

[c]See text for references for each solvent.

Table 42. Mole fraction solubilities of nitrogen in six alcohols

at 0.101325 MPa partial pressure of nitrogen, $10^4 x_1$

T/K	2-Methyl-1-Propanol	1-Pentanol	1-Octanol	1-Decanol
273.15	4.86			
278.15	4.86			
283.15	4.85		5.97	6.42
288.15	4.85		6.10	6.50
293.15	4.84	5.14	6.23	6.58
298.15	4.84	5.27	6.35	6.65
303.15	4.83	5.39	6.48	6.73
308.15	4.83	5.52	6.60	6.80
313.15	4.82		6.72	6.87
318.15	4.82			
323.15	4.81			
328.15	4.81			
$A_0{}^a$	-7.69430	-6.0966	-6.18842	-6.65033
$A_1{}^a$	0.179798	-4.3302	-3.49654	-1.98173
σ^b	0.014	0.047	0.044	0.0029

1 - Hexanol at 298.15 K, $10^4 x_1$ = 5.84 [118].

1 - Heptanol at 298.15 K, $10^4 x_1$ = 6.10 [118].

^{a} Coefficients in Eq. (5).

^{b} Standard deviation in ln x_1.

^{c} See text for references for each solvent.

a group and individually. 2-Propanone, acetic acid(methyl ester), and 1,1'-oxybisethane are also discussed individually.

4.9.a. Alcohols as a Group

Each of the 1-alkanols from methanol to 1-decanol has been investigated by more than one research group except for 1-nonanol. 2-Propanol was investigated by only one group. 1-Hexanol and 1-heptanol were studied only at 298.15 K, but the other alcohols were studied as a function of temperature. Smoothed values of the mole fraction solubilities are presented in Tables 41 and 42.

For the 1-alkanols all of the original data were fit as a function of τ and the number of carbon atoms C to obtain

$$\ln x_1 = -15.017 + 8.9896/\tau$$

$$+ 3.5195 \ln \tau + 0.103\ 30C, \tag{69}$$

with a standard deviation of 0.094 in ln x_1. Individual data points differing by more than two standard deviations from the smoothed values were deleted and the remaining points were refitted. For the 1-alkanols, the nitrogen solubility increases with the number of carbons (see Fig. 6).

Nitrogen solubility in 1-nonanol, 1-undecanol, 1-dodecanol, cyclohexanol, and ethylene glycol were studied by only one group each. Only methanol and ethanol were studied at higher pressures; these will be considered in Secs. 4.10.a. and 4.10.b. In the following sections, brief descriptions of the original data are given for each alcohol.
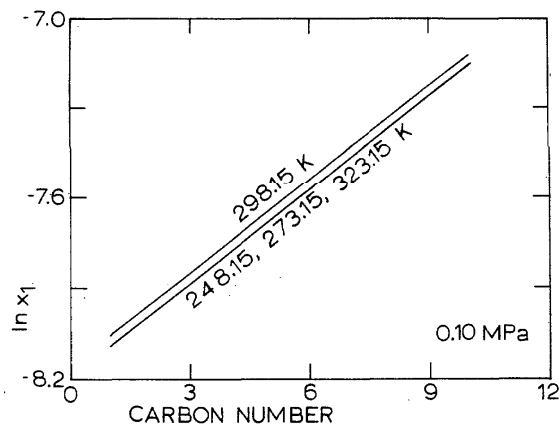
FIG. 6. Mole fraction solubility of nitrogen in the 1-alkanols at 0.101 325 MPa as a function of carbon number.

4.9.b. Methanol

Five groups studied nitrogen solubility in methanol. Kretschmer et al.[52] studied the solubility in the temperature range 248.15–323.15 K. Katayama and Nitta[64] studied it in the temperature range 213.15–298.15 K. The agreement between these two groups is satisfactory. Boyer and Bircher's value at 298.15 K[118] was also used to obtain smoothed values. Just's values[51] which were too low and Makranczy et al.'s value[119] which was too high were rejected.

4.9.c. Ethanol

Six groups have studied this system. Just's values[51] and Metschl's value[120] were too low. Makranczy et al.'s value[119] was too high. The data by Kretschmer et al.[52] and by Katayama and Nitta[64] and the datum by Boyer and Bircher[118] were used to obtain the smoothed values.

4.9.d. 1-Propanol

Four groups have studied this system. Makranczy et al.'s value[119] was too high and Boyer and Bircher's value at 308.15 K[118] was also too high. Katayama and Nitta's values,[64] Gjaldbaek and Niemann's value at 298.06 K,[121] and the value of Boyer and Bircher at 298.15 K[118] were used to obtain the smoothed values.

4.9.e. 2-Propanol

This system was studied by Kretschmer et al.,[52] and Katayama and Nitta.[64] All of their data were used to obtain the smoothed values.

4.9.f. 1-Butanol

This system was studied by four groups: Kretschmer et al.,[52] Katayama and Nitta,[64] Boyer and Bircher,[118] and Makranczy et al.[119] All of their data were used to obtain the smoothed values.

4.9.g. 2-Methyl-1-propanol

This system was only studied by Battino et al.[122] and in the temperature range 274.02–327.96 K. All six values were used to obtain the smoothed values.

4.9.h. 1-Pentanol

This system was studied by four groups, viz., Just,[51] Gjaldbaek and Niemann,[121] Boyer and Bircher,[118] and Makranczy et al.,[119] but with widely varying results and in the narrow temperature range 293–308 K. The smoothed values obtained by using all of their data must be regarded as tentative.

4.9.i. 1-Hexanol

This system was studied by two groups and only at 298.15 K. Makranczy et al.'s value for $10^4\, x_1$ is 5.99,[119] while Boyer and Bircher's value is 5.84.[118]

4.9.j. 1-Heptanol

This system was studied by three groups and only at 298.15 K. Makranczy et al.'s value $(10^4\, x_1 = 6.60)$[119] is higher than Boyer and Bircher's value $(10^4\, x_1 = 6.10)$[118] and Ijams' value $(10^4\, x_1 = 6.09)$.[68]

4.9.k. 1-Octanol

This system was studied by four groups, but with widely varying results. Makranczy et al.'s value[119] was too high. All the data of the other three groups, viz., Ijams,[68] Boyer and Bircher,[118] and Wilcock et al.,[69] were used to obtain the smoothed values. However, the smoothed results should be considered tentative.

4.9.l. 1-Decanol

Two groups studied this system. Makranczy et al.'s value[119] was judged to be too high. Three values of Wilcock et al.[69] in the temperature range 283–313 K were used to obtain the smoothed values.

4.9.m. 1-Nonanol, 1-Undecanol, and 1-Dodecanol

Only Makranczy et al.[119] studied these systems. Their values for $10^4\, x_1$ are 7.50, 8.49, and 8.98 for 1-nonanol, 1-decanol, and 1-dodecanol, respectively, at 298.15 K. Their values in other solvents are consistently higher than other groups' values, and these results should be considered tentative.

4.9.n. Cyclohexanol and 1,2-Ethanediol (Ethylene Glycol)

Only Gjaldbaek and Niemann studied these systems.[121] Their value for $10^4\, x_1$ is 2.66 for cyclohexanol at 298.15 K, and 0.342 and 0.356 for 1,2-ethanediol at 298.16 and 298.17 K, respectively. The values should be considered tentative.

4.9.o. 2-Propanone (Acetone)

Three groups studied this system. The two data points obtained by Just[51] were too low. The seven data points of Horiuti in the temperature range 195–314 K[79] and the three data points of Kretschmer et al.[52] in the temperature range

Table 43. Mole fraction solubilities of nitrogen in 2-propanone (acetone) at 0.101325 MPa pressure of nitrogen

T/K	$10^4\, x_1$	T/K	$10^4\, x_1$
193.15	3.891	273.15	4.955
203.15	3.979	283.15	5.135
213.15	4.083	293.15	5.324
223.15	4.200	298.15	5.421
233.15	4.330	303.15	5.520
243.15	4.471	313.15	5.726
253.15	4.623	323.15	5.939
263.15	4.784		

248–298 K gave the following least-squares equation:

$$\ln x_1 = -11.3529 + 3.775\,45/\tau + 2.349\,33\ln\tau, \quad (70)$$

with a standard deviation in the mole fraction of 3.2×10^{-6}. Smoothed values at 10 K intervals are given in Table 43.

4.9.p. Acetic Acid, Methyl Ester (Methyl Acetate)

Only Horiuti[79] studied this system in the temperature range 194–313 K. Eleven data points gave the following equation:

$$\ln x_1 = -10.3409 + 2.3823/\tau + 1.9228\ln\tau, \quad (71)$$

with a standard deviation about the regression line of 1.6×10^{-6} in x_1.

Table 44. Mole fraction solubilities of nitrogen in twelve organic compounds containing oxygen at 0.101325 MPa partial pressure of nitrogen

Solvent	T/K	$10^4\, x_1$	Reference
Cyclohexanone	293.15	3.72	[66]
	298.15	3.77	[66]
Acetic acid	293.15	2.79	[51]
	298.15	2.80	[51]
2-Methylpropanoic acid	298.20	6.54	[53]
Acetic acid, ethyl ester	293.15	6.83	[51]
	298.15	6.95	[51]
Acetic acid, 2-methylpropyl ester	293.15	9.39	[51]
	298.15	9.47	[51]
Acetic acid, pentyl ester	293.15	9.35	[51]
	298.15	9.43	[51]
Tetrahydrofuran	293.15	5.07	[51]
	298.15	5.21	[51]
1,4-Dioxane	293.15	2.29	[66]
	298.15	2.37	[66]
2,3-Dihydropyran	293.15	4.90	[66]
	298.15	4.93	[66]
Tetrahydro-2H-pyran	293.15	5.77	[66]
	298.15	5.93	[66]
1,1'-Oxybispropane	293.15	12.0	[66]
	298.15	12.2	[66]
1,2-Epoxyethane	273.2	3.57	[123]
	298.2	4.59	[123]
	323.2	5.49	[123]

4.9.q. 1,1-Oxybisethane (Diethyl Ether)

Christoff[40] studied this system only at 273.15 K; his value for the mole fraction solubility is 1.16×10^{-3} and is in fairly good agreement with the values of 1.199×10^{-3} at the same temperature obtained by Horiuti[79] who studied this system in the temperature range 195–293 K. Horiuti's six data points gave the following equation

$$\ln x_1 = -6.5838 - 0.3980/\tau, \tag{72}$$

with a standard error about the regression line of 2.3×10^{-5} in x_1.

4.9.r. Other Organic Compounds Containing Oxygen

Other organic compounds containing oxygen were studied only at one or two temperatures and by only one group each. The mole fraction solubility for these solvents is in Table 44, but all of these values must be considered tentative.

4.10. Nitrogen in Organic Compounds Containing Oxygen (above 0.101 325 MPa)

Every system in this section has been studied by only one group. The results should be considered tentative.

4.10.a. Methanol

Nitrogen solubilities in methanol at higher pressures than atmospheric were studied by Krichevskii and Lebedeva[124] in the temperature range 273 to 343 K and pressure range 4.9 to 28.4 MPa. Their results and the values at 0.101 325 MPa gave the following result with a standard deviation in $\ln x_1$ of 0.025:

$$\ln x_1 = -15.9839 + 13.2246/\tau$$
$$+ 5.0932 \ln \tau - 0.003\ 272\ 4(P/\text{MPa})$$
$$+ 0.966\ 73 \ln(P/\text{MPa}). \tag{73}$$

4.10.b. Ethanol

The nitrogen/ethanol system at higher pressures than atmosphere was studied by Frolich et al.[98] and only at 298.15 K. Their data and the smoothed value at 0.101 325 MPa gave the following results

$$\ln x_1 = -5.8534 + 0.907\ 15 \ln(P/\text{MPa}), \tag{74}$$

with a standard deviation of 0.012 in $\ln x_1$. The combined data gave

$$\ln x_1 = -9.9399 + 5.4296/\tau$$
$$+ 2.0716 \ln \tau + 0.908\ 33 \ln(P/\text{MPa}). \tag{75}$$

with standard deviation in $\ln x_1$ of 0.010.

4.10.c. Cyclohexanone

This system was studied by Khodeeva and Dymova[59] in the temperature range 348–473 K and the pressure range 2.4–9.7 MPa. Their data were smoothed and gave the following results:

$$\ln x_1 = -7.1580 + 1.4563 \ln \tau$$
$$+ 0.952\ 92 \ln(P/\text{MPa}), \tag{76}$$

with standard deviation of 0.040 in $\ln x_1$.

4.10.d. 1,3-Dioxolan-2-one, 4-methyl-, (Propylene Carbonate)

This system was studied by Shakhova et al.[125] in the temperature range 283–323 K and the pressure range 6.3–12.5 MPa. Their data gave the equation:

$$\ln x_1 = -8.0540 + 1.5329 \ln \tau + 0.89095 \ln(P/\text{MPa}), \tag{77}$$

with standard deviation of 0.012 in $\ln x_1$.

4.10.e. 1,2,3-Propanetriol, triacetate (Glycerol Triacetate)

This system was studied by Shakhova et al.[125] in the temperature range 288–323 K and the pressure range 6.8–14.7 MPa. Their data gave the equation:

$$\ln x_1 = -141.148 + 190.356/\tau$$
$$+ 65.768 \ln \tau + 0.922\ 54 \ln(P/\text{MPa}), \tag{78}$$

with standard deviation of 0.026 in $\ln x_1$.

4.10.f. Pentanedioic Acid, -Dimethyl Ester (Dimethyl Glutarate)

This system was studied by Shakhova et al.[125] only at 313.15 K and pressure range 5.6–14.2 MPa. Their results gave the equation:

$$\ln x_1 = -5.2975 + 0.917\ 48 \ln(P/\text{MPa}), \tag{79}$$

with a standard deviation of 0.017 in $\ln x_1$.

4.10.g. 2,5,8,11,14-Pentaoxapentadecane (Tetramethylene Glycol Dimethyl Ester)

This system was studied by Zubchenko and Shakhova[126] only at 313.15 K and the pressure range 2.8–14.0 MPa. Their results gave

$$\ln x_1 = -5.1871 + 0.929\ 43 \ln(P/\text{MPa}), \tag{80}$$

with a standard deviation of 0.021 in $\ln x_1$.

4.10.h. 1,2-Epoxyethane (Ethylene Oxide)

This system was studied by Hess and Tilton[127] at 303 and 318 K, and at three different pressures each. Their mole fraction solubilities at 303 K are 0.0003, 0.0016, and 0.0030 at 0.21, 0.28, and 0.34 MPa, respectively; their mole fraction solubilities at 318 K are 0.0017, 0.0028, and 0.0039 at 0.34, 0.41, and 0.48 MPa, respectively.

4.11. Nitrogen in Organic Compounds Containing Halogen (0.101 325 MPa)

The solubility of nitrogen in halogen containing organic solvents varies a great deal, e.g., the mole fraction solubility at 0.101 325 MPa partial pressure is 4.27×10^{-4} in chlorobenzene and is 5.11×10^{-3} in perfluoro-1-isopropoxy hexane, both at 298.15 K. The enthalpy of solution is positive in chlorobenzene ($\Delta \bar{H}_1^\circ = 2619$ J mol^{-1} at 298.15 K) and in carbon tetrachloride ($\Delta \bar{H}_1^\circ = 2467$ J mol^{-1} at 298.15 K), but is negative in perfluoro-1-isopropoxyhexane ($\Delta \bar{H}_1^\circ = -1977$ J mol^{-1} at 298.15 K). The smoothed values are shown in Table 45. However, most of the systems have been studied by only one group each and the results should be considered tentative.

Table 45. Mole fraction solubilities of nitrogen in organic compounds containing halogen at 0.101325 MPa partial pressure of nitrogen

Solvent	$10^4 x_1$ 288.15K	298.15K	308.15K	A_0^a	A_1^a	A_2^a	$10^4 \sigma^b$	Temperature range studied/K
CCl_2F_2	17.4c	17.8c	18.2c					199-276
CCl_4	6.197	6.40	6.625	-11.30302	4.07891	2.3634	0.009	253-333
$CHCl_3$	4.04c	4.42	4.81c					293-298
$C_2Cl_2F_4$ d	98.	73.	56.					293-333
$C_2Cl_3F_3$ e	19.43	19.58	19.72	-6.017	-0.6519		0.16	277-308
C_6F_6 f	17.96	17.95	17.94c	-6.3362	0.0405		0.09	282-297
C_6H_5Cl g	4.121	4.268	4.423	-12.41926	4.99558	2.73200	0.018	233-353
$C_6H_{13}Cl$ h	7.85c	8.19	8.52c					293-298
C_7F_{14} i		33.1						298
C_7F_{16} j	39.4	39.0	38.7	-5.8175	0.8081		0.2	275-321
$C_7H_{15}Br$ k		6.75						298
C_8F_{16} l	31.9°	31.9	31.9	-5.7811	0.0988		0.1	296-320
C_9F_{20} m	52.5c	51.1	49.8	-6.0684	2.3613		0.1	298-323
$C_{10}F_{22}O_2$ n	51.2c	50.0	48.9	-5.9621	1.9787		0.1	298-323

a Coefficients in Eq. (5).

b Standard deviation in x_1.

c Extrapolated values.

d 1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114).

e 1,1,2-Trichloro-1,2,2-trifluoroethane.

f Hexafluorobenzene

g Chlorobenzene

h 1-Chlorohexane

i Undecafluoro(trifluoromethyl)cyclohexane (perfluoromethylcyclohexane)

j Hexadecafluoroheptane (perfluoroheptane)

k 1-Bromoheptane

l Decafluorobis(trifluoromethyl)cyclohexane (perfluordimethylcyclohexane); isomer not specified.

m 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethoxy]-hexane (perfluoro-1-isopropoxy hexane).

n 1,1,2,2,3,3,4,4-Octafluoro-1,4-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethoxy]butane (perfluoro-1,4-diisopropoxy butane).

4.11.a. Dichlorodifluoromethane (Freon-12)

Steinberg et al.[128] studied this system in the temperature range 199–276 K. Their results show a minimum in the solubility somewhere between 203 and 243 K. Because of the scatter of the data points, only four values in the temperature range 243–276 K were fitted and gave

$$\ln x_1 = -5.6588 - 2.0085/T, \qquad (81)$$

with standard deviation of 6.3×10^{-5} in x_1. The extrapolated values are in Table 45. Those who are interested in the lower temperature region should consult the original paper.

4.11.b. Tetrachloromethane

Horiuti[79] studied this system in the temperature range 253–333 K. The five data points gave the coefficients and standard deviation listed in Table 45. The values for $\Delta \overline{G}_1^{\circ}/$ kJ mol^{-1}, $\Delta \overline{H}_1^{\circ}/J$ mol^{-1}, and $\Delta \overline{S}_1^{\circ}/J$ K^{-1} mol^{-1} are 18.228, 2467, and −52.86, respectively, at 298.15 K.

4.11.c. Trichloromethane (Chloroform)

Just[51] measured the solubility at 293.15 and 298.15 K. Körösy[129] measured it at 295.15 K, his value being 2.1%

lower than Just's value at the same temperature. The three values were used to obtain the smoothed values, two of them being extrapolated ones.

4.11.d. 1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)

Williams[130] studied this system at 293, 313, and 333 K. The temperature dependence of the solubility is abnormally great compared to that in other solvents.

4.11.e. 1,1,2-Trichloro-1,2,2-trifluoroethane

Hiraoka and Hildebrand[131] studied this system in the temperature range 277–308 K. Four data points gave the coefficients listed in Table 45.

4.11.f. Hexafluorobenzene

Evans and Battino[132] studied this system in the temperature range 282–297 K. Four data points gave the coefficients listed in Table 45.

4.11.g. Chlorobenzene

Horiuti[79] studied this system in the temperature range 233–353 K. The seven data points gave the coefficients and standard deviation listed in Table 45. The values for $\Delta \overline{G}_1^{\circ}/$ kJ mol^{-1}, $\Delta \overline{H}_1^{\circ}/J$ mol^{-1}, and $\Delta \overline{S}_1^{\circ}/J$ K^{-1} mol^{-1} are 19.234, 2619, and −55.73, respectively, at 298.15 K.

4.11.h. 1-Chlorohexane

Guerry[66] measured the solubility at 293.15 and 298.15 K. The two data points were extrapolated to obtain the values at 288.15 and 308.15 K.

4.11.i. Undecafluoro (trifluoromethyl) cyclohexane (Perfluoromethylcyclohexane)

Gjaldbaek and Hildebrand[63] measured the solubility at 298.05 and 298.15 K. These points differed by 3.3%. The average of the two values is in Table 45.

4.11.j. Hexadecafluoroheptane (Perfluoroheptane)

Gjaldbaek and Hildebrand[63] studied this system in the temperature range 275–321 K. The eight data points gave the coefficients in Table 45.

4.11.k. 1-Bromoheptane

Only one datum by Ijams[68] at 298.15 K is available.

4.11.l. Decafluorobis(trifluoromethyl)cyclohexane (Perfluorodimethylcyclohexane)

Gjaldbaek and Hildebrand[63] studied this system in the temperature range 298–320 K. The four data points gave the coefficients in Table 45.

4.11.m. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethoxy]-hexane (Perfluoro-1-isopropoxyhexane)

Tham et al.[133] studied this system in the temperature range 298–323 K. The five data points gave the coefficients in Table 45.

4.11.n. 1,1,2,2,3,3,4,4-Octafluoro-1,4-bis(1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethoxy)butane (Perfluoro-1,4-diisopropxybutane)

Tham et al.[133] studied this system in the temperature range 298–323 K. The five data points gave the coefficients in Table 45.

4.11.o. Methane, chlorotrifluoro

Leites and Adlivankina[134] studied this system in the temperature range 93–123 K. The Ostwald coefficients are 0.146, 0.157, 0.143, and 0.132 at 93, 103, 113, and 123 K, respectively.

4.11.p. Tetrafluoromethane

Leites and Adlivankina[134] studied this system in the temperature range 93–123 K. The Ostwald coefficients are 0.118, 0.087, 0.057, and 0.030 at 93, 103, 113, and 123 K, respectively.

4.11.q. Germanium Tetrachloride

Gorbachev and Tret'yakov[135] measured the nitrogen solubility in germanium tetrachloride at 293 K. The Ostwald coefficient is 0.208.

4.11.r. Other Organic Compounds Containing Halogen

Tham et al.[133] studied the nitrogen/FC-80 system in the temperature range 298–323 K. Sargent and Seffl[136] studied the same system at 298 and 310 K. FC-80 is a mixture of isomers of heptafluorotetrahydro(nonafluorobutyl)furan (perfluorobutylperfluorotetrahydrofuran). Sargent and Seffl[136] studied the nitrogen/L-1822 system at 298 and 310 K. L-1822 is a mixture of mostly 10-carbon fluorocarbons. Those who are interested in these systems should consult the original papers.

4.12. Nitrogen in Organic Compounds Containing Halogen (above 0.101 325 MPa)

The solubility of nitrogen was studied in five halogen-containing solvents at pressures above 0.1 MPa. Two groups studied the solubility in chlorodifluoromethane at comparable temperatures and pressures. Other solvent systems were studied by only one group each, and the results should be considered tentative.

4.12.a. Chlorotrifluoromethane (Freon-13)

Chaikovskii et al.[137] studied this system in the pressure range 3.0–9.5 MPa and at 233.15 and 258.15 K. Their data gave the following result:

$$\ln x_1 = -4.9416 + 3.4379/\tau + 1.1938 \ln(P/\text{MPa}),$$
$$(82)$$

with a standard deviation of 0.037 in $\ln x_1$.

4.12.b. Dichlorodifluoromethane

Maslennikova et al.[138] studied this system at three temperatures, i.e., 295.15, 323.15, and 348.15 K and in the pressure range 2.5–17.8 MPa. Their data gave the following re-

sult:

$$\ln x_1 = -3.9922 - 2.7246/\tau + 1.5036 \ln(P/\text{MPa}),$$
$$(83)$$

with a standard deviation of 0.13 in $\ln x_1$.

4.12.c. Tetrachloromethane

Frolich et al.[98] studied this system at 298.15 K in the pressure range 1.0–12.0 MPa. Their data gave the following result at 298.15 K:

$$\ln x_1 = -5.0973 + 0.9897 \ln(P/\text{MPa})$$
$$-0.004\,275(P/\text{MPa}),\qquad(84)$$

with a standard deviation of 0.0025 in $\ln x_1$.

4.12.d. Tetrafluoromethane

Chaikovskii et al.[137] studied this system at three temperatures, i.e., 193.15, 198.15, and 203.15 K in the pressure range 3.4–6.2 MPa. Their data gave the following result:

$$\ln x_1 = -6.6987 + 5.7636/\tau + 1.6315 \ln(P/\text{MPa})$$
$$(85)$$

with a standard deviation of 0.034 in $\ln x_1$.

Eckert and Prausnitz[139] studied this system in the lower pressure range, i.e., 0.03–0.19 MPa and in the temperature range 70–116 K. Fitting their data gave

$$\ln x_1 = -9.0593 + 9.3616/\tau + 1.6578 \ln(P/\text{MPa}),$$
$$(86)$$

with a standard deviation of 0.32 in $\ln x_1$. Combining both sets of data yielded

$$\ln x_1 = -8.2643 + 8.7357/\tau + 1.6672 \ln(P/\text{MPa}),$$
$$(87)$$

with a standard deviation of 0.15 in $\ln x_1$.

4.12.e. Chlorodifluoromethane

This system has been studied by two different groups. Maslennikova et al.[138] studied it at three temperatures, i.e., 295.15, 313.15, and 333.15 K in the pressure range 2.5–19.5 MPa. Nohka et al.[140] studied the same system at four temperatures, i.e., 273.15, 298.15, 323.15, and 348.15 K in the pressure range 2.5–21.5 MPa. The combined data gave the following results:

$$\ln x_1 = 43.7761 - 70.4042/\tau$$
$$-23.2335 \ln \tau + 1.5510 \ln(P/\text{MPa}),\qquad(88)$$

with a standard deviation of 0.34 in $\ln x_1$.

4.13. Nitrogen in Solvents Containing Nitrogen (0.101 325 MPa)

In most of the solvents of this section, the nitrogen solubilities were studied by only one group each. Exceptions are nitrobenzene, benzenamine, and 1,1,2,2,3,3,4,4,4-nonafluoro-N,N-bis(nonafluorobutyl)-1-butanamine systems, where the solubilities were measured by two or three groups each but without satisfactory agreement. So, all the data should be considered tentative. The mole fraction solubilities at one temperature (mostly at 298.15 K) are shown in

Table 46. Mole fraction solubilities of nitrogen in

solvents containing nitrogen at 0.101325 MPa partial pressure

of nitrogen

Solvent	$10^4 \, x_1{}^a$
Nitromethane	2.01
N-Methylacetamide	2.46[b]
Nitric acid, propyl ester	5.9[c]
Pyrrolidine	3.68
Pyridine	2.50
Piperidine	4.22
Nitrobenzene	2.64
Benzenamine	1.23
$(C_4F_9)_3N$[d]	39.6

[a] At 298.15 K unless otherwise noted.

[b] At 308.15 K. The solubility data are available between

308.15 and 343.15 K; see text.

[c] At "room" temperature.

[d] 1,1,2,2,3,3,4,4,4-Nonafluoro-N,N-bis(nonafluorobutyl)-1-

butanamine. For the solubility between 283 and 318 K, see text.

Table 46. These solubilities were determined at only 298.15 K or at 293.15 and 298.15 K except in the case of N-methylacetamide and 1,1,2,2,3,3,4,-4,4-nonafluoro-N,N-bis(nonafluorobutyl)-1-butanamine where the solubilities were determined over a wider temperature range. In Table 47, nitrogen solubilities in hydrazine and its derivatives are shown as a function of temperature. For the solvents in this section, the mole fraction solubility changes by a factor of 550 from the least soluble solvent (hydrazine) to the most soluble solvent $[(C_4F_9)_3N]$.

Table 47. Mole fraction solubilities of nitrogen in hydrazine, methylhydrazine, and 1,1-dimethylhydrazine at 0.101325 MPa partial pressure of nitrogen

T/K	$10^4 \, x_1$		
	Hydrazine	Methylhydrazine	1,1-Dimethylhydrazine
258.15		0.687	3.04
268.15		0.745	3.22
278.15	0.054	0.803	3.41
288.15	0.062	0.861	3.58
298.15	0.072	0.918	3.76
308.15	0.082		

4.13.a. Nitromethane

Only Friedman[141] measured the solubility of nitrogen in nitromethane and at 298.15 K.

4.13.b. N-Methylacetamide

Wood and DeLaney[142] studied this system. Between 308 and 343 K, the mole fraction solubility is expressed by

$$\ln x_1 = -7.514 - 2.457/\tau. \tag{89}$$

4.13.c. Nitric Acid, Propyl Ester

Amster and Levy[143] studied this system at "room temperature." Values of pressure and solubility were read from a graph in their paper, and the mole fraction solubility at 0.101 325 MPa partial pressure of nitrogen was estimated to be $(5.9 \pm 0.7) \times 10^{-4}$.

4.13.d. Pyrrolidine, Pyridine, and Piperidine

Guerry[66] measured the solubility of nitrogen in these three solvents at 293.15 and 298.15 K. His values at 298.15 K are listed in Table 46. The values for $10^4 \, x_1$ at 293.15 K are 3.54, 2.41, and 4.13 for pyrrolidine, pyridine, and piperidine, respectively.

4.13.e. Nitrobenzene

Just[51] studied this system at 293.15 and 298.15 K and Metschl[120] studied the same system at 298.15 K. Metschl's value at 298.15 K $(10^4 \, x_1 = 2.6)$ is in agreement with Just's value at the same temperature $(10^4 \, x_1 = 2.64)$ which is listed in Table 46. Just's value at 293.15 K is 2.60 for $10^4 \, x_1$.

4.13.f. Benzenamine (Aniline)

Just[51] studied this system at 293.15 and 298.15 K and Metschl[120] studied the same system at 298.15 K. At 298.15 K, Metschl's value $(10^4 \, x_1 = 1.3)$ is 13% higher than Just's value $(10^4 \, x_1 = 1.15)$. The average of the two values is listed in Table 46. Just's value for $10^4 \, x_1$ is 1.13 at 293.15 K.

4.13.g. 1,1,2,2,3,3,4,4,4-Nonafluoro-N-N-bis(nonafluorobutyl)-1-butanamine (Perfluorotributylamine)

Kobatake and Hildebrand[144] measured the solubility of nitrogen in this solvent in the temperature range 283–303 K. Their data are expressed by

$$\ln x_1 = -5.9155 + 0.768 \, 21/\tau, \tag{90}$$

which gives 34.90 for $10^4 \, x_1$ at 298.15 K.

Sargent and Seffl[136] studied this system at 298.15 and 310.15 K. Their value at 298.15 K $(10^4 x_1 = 41.6)$ (calculated from Ostwald coefficient by using 360 $cm^3 \, mol^{-1}$ for the molar volume of $[C_4F_9(_3N)]$ is 19% higher than Kobatake and Hildebrand's value at the same temperature. Powell[145] studied the same system in the temperature range 288.15–318.15 K, giving only the solubility value at 298.15 K and a smoothing equation. His value at 298.15 K $(10^4 \, x_1 = 42.36)$ is 21% higher than Kobatake and Hildebrand's value. The average of the three values at 298.15 K is listed in Table 46. This system definitely needs further investigation.

4.13.h. Hydrazine, Methylhydrazine, and 1,1-Dimethylhydrazine

Chang et al.[146] studied the solubility of nitrogen in these solvents. They studied the hydrazine system at three temperatures between 278.15 and 308.18 K; the data are expressed by

$$\ln x_1 = -7.7956 - 12.0646/\tau. \tag{91}$$

The smoothed data are listed in Table 47. They studied the methylhydrazine system at three temperatures between 253.24 and 298.14 K; the data are expressed by

$$\ln x_1 = -7.422 - 5.5858/\tau, \tag{92}$$

and the smoothed data are listed in Table 47. They studied 1,1-dimethylhydrazine at three temperatures between 253.05 and 293.16 K; the data are expressed by

$$\ln x_1 = -6.5297 - 4.0466/\tau. \tag{93}$$

4.13.i. 1,2-Dimethylhydrazine

Chang et al.[146] gave an estimated equation for the Gibbs energy for dissolving nitrogen in this solvent (without doing experimental measurements but by using logical assumptions). The equation gives 15.4 for $10^4 x_1$ at 298.15 K.

4.14. Nitrogen in Solvents Containing Nitrogen (above 0.101 325 MPa)

Only two solvents have been studied in this section and by only one group.

4.14.a. Pyrrolidinone, 1-methyl-

Shakhova et al.[125] studied this system at three temperatures between 283.15 and 333.15 K and in the pressure range 4.3–13.5 MPa. Smoothing the data gave

$$\ln x_1 = -4.8242 - 4.2435/\tau + 0.9431 \ln(P/\text{MPa}), \tag{94}$$

with a standard deviation of 0.023 in $\ln x_1$.

4.14.b. 2-Pyrrolidinone,1,5-dimethyl-

Shakhova et al.[125] studied this system at three temperatures between 283.15 and 323.15 K and in the pressure range 7.5 to 14.2 MPa. Smoothing the data gave

$$\ln x_1 = -4.2576 - 4.2542/\tau + 0.8523 \ln(P/\text{MPa}), \tag{95}$$

with a standard deviation of 0.017 in $\ln x_1$.

4.15. Nitrogen in Organic Compounds Containing Sulfur or Silicon

Recommended values are given for solubilities in carbon disulfide. Other solvent systems have been studied by only one group each, and the results are classed as tentative. Only carbon disulfide and octamethylcyclotetrasiloxane have been studied in a wider temperature range. The other solvents were studied at a 5 K or narrower range. The sulfur hexafluoride system was studied at higher pressures.

Table 48. Mole fraction solubilities of nitrogen in carbon disulfide and octamethylcyclotetrasiloxane at 0.101325 MPa partial pressure of nitrogen

T/K	$10^4 x_1$	
	Carbon disulfide	OMCTS[a]
278.15	1.922	
283.15	1.995	
288.15	2.068	
293.15	2.142	25.4
298.15	2.215	25.5
303.15	2.288	25.6
308.15		25.6
313.15		25.7

[a] Octamethylcyclotetrasiloxane

4.15.a. Carbon Disulfide

Four groups studied this system. Gjaldbaek and Hildebrand[63] measured the solubility at 298.04 and 298.11 K; Kobatake and Hildebrand[144] reported the solubility at four temperatures between 279 and 304 K; and Powell[145] gave the value at 298.15 K along with the coefficient of the temperature dependence between 273 and 318 K. Kobatake and Hildebrand's values gave the following result

$$\ln x_1 = -6.4402 - 5.8881/\tau, \tag{96}$$

with a standard deviation of 2.01×10^{-7} in x_1. Values of the other two papers agree with those obtained from Eq. (96) within 0.7%. Just's[51] values at 293.15 and 298.15 K are 34% to 38% lower and were rejected. Recommended values were obtained from Eq. (96) and are shown in Table 48.

4.15.b. Sulfinylbismethane (Dimethyl Sulfoxide)

Only Dymond[72] studied this system. His value for the mole fraction solubility is 8.33×10^{-5} at 298.15 K and 0.101 325 MPa partial pressure of nitrogen.

4.15.c. Sulfur Hexafluoride

Miller et al.[147] measured the solubility of nitrogen in liquid sulfur hexafluoride at 300 K and at 2.5 to 3.0 MPa total pressure of the system. Those who are interested in this system should see the original paper.

4.15.d. Octamethylcyclotetrasiloxane

Wilcock et al.[148] studied this system in the temperature range 292–313 K. Their seven data points gave

$$\ln x_1 = -5.823 - 0.443/\tau, \tag{97}$$

with a standard deviation of 5.5×10^{-5} in x_1. The smoothed solubility values are given in Table 48.

4.15.e. Methyltrichlorosilane and Silicon Tetrachloride

Gorbachev and Tret'yakov[135] measured the nitrogen solubilities in these two solvents by gas chromatography. The Ostwald coefficients at 293 K are 0.187 and 0.225 for methyltrichlorosilane and silicon tetrachloride, respectively.

4.16. Biological Fluids

The solubility of nitrogen has been determined in a variety of fluids present in or derived from living organisms. (See Ref. 1 for a comprehensive set of data sheets on these systems.) In this section, we report on solubilities in several grouped systems and in olive oil. It should be understood that in this paper we can only give brief descriptions of the fluids, partially for reasons of space but mostly because they are not well characterized even in the original papers.

4.16.a. Solubility in Some Oils and Lard

Table 49 gives the Bunsen coefficient solubilities in a group of oils and lard. These values would all be considered to be tentative and are of the order of 2%–5% in precision.

4.16.b. Solubility in Olive Oil

The solubility of nitrogen in olive oil was studied by four groups.[152-155] However, the single value determined by Ikels[153] is much too low compared to the other results and is rejected. Tentative smoothed values were obtained by least-squares treatment to yield the following results in terms of the mole fraction solubility at 0.101 325 MPa partial pressure of gas x_1 and the Ostwald coefficient L:

$$\ln x_1 = -5.6757 - 0.58383/\tau, \tag{98}$$

$$L = 1.9886 \times 10^{-3} + 2.3052 \times 10^{-4}(T/K). \tag{99}$$

The standard deviation of the smoothed data was 3.1% at

Table 49. Bunsen coefficients for nitrogen solubilities in several oils and lard

Fluid	T/K	Bunsen Coefficient α
Corn oil	296-9	0.0631[a]
	318	0.0633[a]
Cottonseed oil	296-9	0.0613[a]
	313	0.062[b]
	318	0.0613[a]
Hydrogenated cotton seed oil	318	0.0670[a]
Steam rendered lard	318	0.0622[a]
Lard	313	0.066[b]
Butter oil	313	0.089[b]
	333	0.079[b]
Soybean oil	303	0.0860[c]
	323	0.0685[c]
	343	0.0522[c]

[a][149] [b][150] [c][151]

Table 50. Nitrogen solubilities in olive oil

T/K	$10^3 \, x_1$[a]	$10^2 \, L$[b]
283.15	2.79	6.73
288.15	2.80	6.84
293.15	2.81	6.96
298.15	2.82	7.07
303.15	2.83	7.19
308.15	2.84	7.30
313.15	2.85	7.42
318.15	2.85	7.53
323.15	2.86	7.65
328.15	2.87	7.76

[a] Mole fraction solubility (0.101325 MPa).

[b] Ostwald coefficient.

the midpoint of the temperature range. Smoothed values are given in Table 50 at 5 K intervals.

4.16.c. Nitrogen Solubilities in Various Human and Animal Fluids

For nitrogen solubilities in various human and animal fluids such as human blood and hemoglobin, ox blood and serum and hemoglobin, fish blood and human urine see Ref. 1.

Farhi et al.[28] determined the solubility of nitrogen in human blood derived from a number of subjects and the averaged value of the Bunsen coefficient at 310.5 K was 0.012 77 at a hematocrit of 45.2. The Bunsen coefficient solubility of nitrogen in human plasma for two subjects determined by the same authors at 310.4 K averaged 0.012 05. Christoforides and Hedley-Whyte[156] determined the solubility of nitrogen in human blood at 298 K (0.0145) and 310 K (0.0139); the Bunsen coefficient is given in parentheses.

Farhi et al.[28] determined the solubility of nitrogen in human urine at 310.5 K for eight subjects whose urine had different specific gravities. The solubility (expressed as the Bunsen coefficient α) decreased as the specific gravity (sp. gr.) increased according to the equation:

$$\alpha = 0.075\ 83 - 0.063\ 35 \text{ sp. gr.,} \tag{100}$$

with an average deviation of 0.4%.

4.16.d. Nitrogen Solubilities in Benzene Solutions of Cholesterol, Cephalin, and Lecithin

Byrne et al.[81] determined the solubility of nitrogen in pure benzene and solutions made up of benzene plus the lipids cholesterol, lecithin, or cephalin at 310.6 K. Table 51 gives averaged values of the Ostwald coefficients for these systems as well as the salting-out parameter k defined in a

Table 51. Nitrogen solubilities in lipid solutions in benzene at 310.6 K

Mass fraction lipid, W_3	Ostwald coeff., L	k^a
0.0	0.1326	
	Cholesterol	
0.0528	0.130	0.19 ± 0.17
0.1069	0.118	0.49 ± 0.09
1.0	0.061^b	
	Lecithin	
0.1993	0.116	0.30 ± 0.04
1.0	0.066^b	
	Cephalin	
0.2003	0.115	0.31 ± 0.05
1.0	0.065^b	

^{a} "Salting-out" parameter $k = (1/W_3) \log (L_o/L_w)$ where L_o and L_w are the nitrogen Ostwald coefficients in benzene and the benzene + lipid solution, respectively.

^{b} Extrapolated nitrogen solubility in the hypothetical pure liquid lipid.

footnote to the table. These authors also extrapolated nitrogen solubilities in the hypothetical pure liquid lipid and found these results to be quite close to the nitrogen solubility in olive oil (see Table 50).

4.16.e. Nitrogen Solubilities in Urea/Water Mixtures

Braun[44] determined the solubility of nitrogen in urea/water mixtures at five temperatures with a precision of about 3%. Least-squares coefficients in terms of weight percent

Table 52. Nitrogen solubilities in urea/water mixtures

T/K	$10^2 A_o{}^a$	$10^4 A_1{}^a$
278.2	2.087	-2.156
283.2	1.960	-2.270
288.2	1.768	-1.907
293.2	1.601	-1.494
298.2	1.413	-0.7804

^{a} Coefficients are for the equation $\alpha = A_o + A_1 W'$ where α is the Bunsen coefficient and W' is the weight percentage of urea in the solution.

Table 53. Nitrogen solubilities in some miscellaneous aqueous solutions of biological interest

Solute^a	T/K	c/mol L^{-1}	$10^2 \alpha$
Glycine	293.3	1.0	1.212
D-Alanine	293.3	1.0	1.213
(R*,R*)=1,2,3,4-Butanetetrol	293.4	1.0	1.321
L-Arabinose	293.4	1.0	1.203
D-Fructose	293.4	1.0	1.221
D-Glucose	293.4	0.25	1.480
	293.4	0.50	1.380
	293.3	1.00	1.215

^{a} From Ref. 21.

urea are given in Table 52. The single temperature (293.3 K) value determined by Hüfner[21] at a urea concentration of 1.0 mol L^{-1} is a Bunsen coefficient of 0.0148 which agrees within 3% with Braun's value.

4.16.f. Nitrogen Solubilities in Some Miscellaneous Biological Solutions

Table 53 gives the solubilities of nitrogen in some miscellaneous aqueous solutions of biological interest.[21]

Shkol'nikova[157] determined the solubility of nitrogen in three gelatin/water solutions as a function of temperature. Least squares for the Bunsen coefficient follow:

1 wt. % gelatin: $\alpha = 65.77 - 0.1786 \, (T/K)$
5 wt. % gelatin: $\alpha = 64.84 - 0.1786 \, (T/K)$
10 wt. % gelatin: $\alpha = 71.24 - 0.2043 \, (T/K)$

Müller[54] determined the solubility of nitrogen in aqueous sucrose solutions at 290.5 K ($\pm$ 0.5 K). A least-squares fit in terms of W', weight percent of sucrose, and the Bunsen coefficient yielded

$$\alpha = 0.016\,32 - 1.952 \times 10^{-4} \, W'.$$

4.17. Miscellaneous Fluids

In this section, we will discuss the solubility of nitrogen in a group of inorganic liquids such as ammonia, carbon dioxide, and some fluorine compounds. See Ref. 1 for nitrogen solubilities in oils, waxes, fuels, hydrocarbon blends, and mixtures.

4.17.a. Compounds Containing Sulfur

Dornte and Ferguson[158] measured the solubility of nitrogen in SO_2 and gave the following equation to $\pm$ 10%:

$$\log_{10} K = 8.729 - 1786/(T/K), \tag{101}$$

where K is the Kuenen coefficient of solubility or cm^3 (STP) of gas dissolved in 1 g of solvent at 0.101 325 MPa partial pressure of gas.

Dean and Walls[159] determined the concentration of nitrogen in both the liquid and gas phases as a function of both temperature and pressure. Their results are presented in Table 54 and the smoothing equation follows:

$$\ln x_1 = -4.3881 - 3.3798/\tau + 0.863\,15 \ln(P/\text{MPa}), \tag{102}$$

Table 54. Mole fraction solubility of nitrogen in sulfur dioxide

T/K	P/MPa	x_{N_2} a	y_{N_2} b
209.26	1.57	0.0051	0.693
241.10	1.83	0.0033	0.972
241.10	3.60	0.0078	0.989
253.15	1.76	0.0055	0.958
301.48	3.60	0.0134	0.849
301.48	3.60	0.0143	0.843

a Liquid phase.   b Vapor phase.   c Ref. 159.

with a standard deviation of 0.35 in $\ln x_1$.

Both Besserer and Robinson[160] and Kalra and Krishnan[161] determined the solubility of nitrogen in hydrogen sulfide as a function of temperature and pressure, but over different ranges: 256–344 K and 1.2–20.7 MPa[160] and 200–228 K and 0.1–13.8 MPa.[161] Both sets of data were combined to yield the following smoothing equation for the mole fraction of nitrogen in the liquid phase:

$$\ln x_1 = -8.6095 + 2.7351 \ln \tau + 1.0389 \ln(P/\text{MPa}),$$ (103)

with a standard deviation of 0.12 in $\ln x_1$.

4.17.b. Nitrogen Oxides

Steinberg et al.[128] measured the solubility of nitrogen in nitrous oxide at ca. atmospheric pressure and from 186 to 244 K. Mole fraction solubilities for smoothing were calculated by us from the original data. Zeininger[185] measured the solubilities for this system in the ranges 213–253 K and 0.6–8.2 MPa. We combined both sets of data and fit them by least squares to yield the following equation:

$$\ln x_1 = -4.1461 - 0.12296 \ln \tau$$
$$+ 0.966\ 17 \ln(P/\text{MPa}),$$ (104)

with a standard deviation of 0.17 in $\ln x_1$.

Chang and Gokcen[162] measured the solubility of nitrogen in nitrogen tetroxide, N_2O_4, from 262 to 303 K and 0.036 to 0.198 MPa. We converted their data to mole fraction solu-

Table 56. Smoothed mole fraction solubilities of nitrogen in carbon dioxide (Eq. (107))

T/K	1.0 MPa	5.0 MPa	10.0 MPa	15.0 MPa
220	0.00319	0.0577	0.201	0.417
230	0.00298	0.0539	0.188	0.389
240	0.00279	0.0504	0.176	0.364
250	0.00261	0.0473	0.165	0.342
260	0.00246	0.0445	0.155	0.321
270	0.00232	0.0420	0.146	0.303
280	0.00219	0.0397	0.138	0.286
290	0.00207	0.0375	0.131	0.271

bilities at 0.101 325 MPa partial pressure of gas and smoothed it to yield:

$$\ln x_1 = -6.106 - 360.31/(T/\text{K}).$$ (105)

The data are considered to be precise to about 5%.

4.17.c. Ammonia

The nitrogen/ammonia system was studied by seven groups[89,162-167] at varying temperatures and pressures. Matous et al.[166] studied the quaternary system argon/methane/nitrogen/ammonia and their work will not be evaluated here. Data from the remaining six papers were processed as a group to yield the following smoothing equation:

$$\ln x_1 = -12.6529 + 5.3410 \ln \tau$$
$$+ 0.886\ 89 \ln(P/\text{MPa}) + 6.0554 \times 10^{-6}(P/\text{MPa})^2.$$ (106)

Smoothed data are presented in Table 55. The standard deviation of the fit in $\ln x_1$ is 0.31.

4.17.d. Carbon Dioxide

Usable data for the nitrogen/carbon dioxide system were published by six groups.[168-173] However, the data of Krichevskii et al.[168] are in poor agreement with those of the

Table 55. Smoothed mole fraction solubilities of nitrogen in ammonia (Eq.(106))

T/K	1.0 MPa	10.0 MPa	100 MPa	200 MPa	300 MPa	380 MPa
200	0.000130	0.00100	0.00818	0.0181	0.0352	0.0603
225	0.000243	0.00188	0.0153	0.0340	0.0660	0.113
250	0.000427	0.00329	0.0269	0.0597	0.116	0.199
275	0.000710	0.00548	0.0448	0.0994	0.193	0.330
300	0.00113	0.00872	0.0713	0.158	0.307	0.526
325	0.00173	0.0134	0.109	0.243	0.470	0.807
350	0.00258	0.0199	0.163	0.360	0.699	-
375	0.00372	0.0287	0.235	0.521	-a	-
400	0.00525	0.0405	0.332	0.735	-	-

a Dash indicates calculated mole fraction greater than 1.0.

Table 57. Coefficients from Eq. (5) for nitrogen solubilities in halogen and boron containing solvents

Solvent	Temp. Range (K)	σ a	A_0	A_1	A_2	B_0
OF_2	145–172	0.24	-0.80575		-5.2865	1.5786
ClF_3	200–283	0.065	-6.0793		0.77385	0.96165
ClF_5	200–283	0.044	-3.8943		-0.29676	1.0099
ClF_6	172–256	0.028	-3.1463		-0.84769	1.0017
FNO_2	172–256	0.10	-3.6435		-1.4293	1.0808
NF_3	133–172	0.053	-6.6655	6.5267		1.1929
N_2F_4	144–228	0.10	-1.4228		-2.4867	0.91034
B_2H_6	144–227	0.087	-2.4149		-1.9013	1.2119
C_3H_9B	200–283	0.047	-4.1357	0.29918		0.98826

a Standard deviation in $\ln x_1$.

other groups. Therefore, the results of the remaining five groups were smoothed together to yield the following equation:

$$\ln x_1 = -4.5185 - 1.5590 \ln \tau + 1.7994 \ln(P/\text{MPa}),$$
(107)

with a standard deviation in $\ln x_1$ of 0.17. Smoothed results for this system are tabulated in Table 56.

4.17.e. Halogen and Boron Containing Solvents

Cannon, Robson, and English[89] made an extensive study of nitrogen solubilities in a number of fluorine containing liquids and two liquid boranes at cryogenic temperatures. Sukhoverkhov et al.[174] were the only other people to study a common system, namely nitrogen/ClF_5. However, Sukhoverkhov et al. presented their solubilities as volume percents and it was not possible to convert their data to mole fractions in the absence of density data. Table 57 contains the coefficients obtained in smoothing the Cannon et al. data according to Eq. (5). The pressure range for all of their work was 2.07 to 4.83 MPa. Temperature ranges are indicated in the table.

5. Air Solubilities

The solubility of air in liquids can be considered to be an ideal linear combination of the solubility of the constituent gases of air in the liquid. Maharajh and Walkley[175] reported that mixtures of gases containing oxygen do not behave independently. This was refuted on theoretical grounds as well as

Table 58. Air solubilities in water calculated by Winkler and smoothed via Eq. (108)

T/K	$10^5 x_1$	Ostwald Coefficient, L
273.15	2.316	0.02882
278.15	2.042	0.02587
283.15	1.824	0.02352
288.15	1.647	0.02151
293.15	1.504	0.01999
298.15	1.388	0.01880
303.15	1.293	0.01778
308.15	1.215	0.01696
313.15	1.151	0.01629
318.15	1.099	0.01576
323.15	1.055	0.01535
328.15	1.020	0.01503
333.15	0.9920	0.01480
338.15	0.9694	0.01464
343.15	0.9521	0.01455
348.15	0.9398	0.01453
353.15	0.9314	0.01456
358.15	0.9268	0.01465
363.15	0.9249	0.01477
368.15	0.9258	0.01493
373.15	0.9305	0.01516
293.15	1.503[a]	0.02003[a]

[a] Ref. 70.

Table 59. Air solubilities in water at elevated pressures as S (cm³(STP) per gram water)

T/K	1.0 MPa	5.0 MPa	10.0 MPa	15.0 MPa	20.0 MPa	25.0 MPa
273.15	0.207	1.165	2.29	3.26	4.06	4.71
278.15	0.187	1.053	2.07	2.95	3.67	4.26
283.15	0.171	0.962	1.89	2.69	3.36	3.89
288.15	0.158	0.887	1.74	2.48	3.09	3.59
293.15	0.147	0.825	1.62	2.31	2.88	3.33
298.15	0.137	0.773	1.52	2.16	2.70	3.12
303.15	0.130	0.729	1.43	2.04	2.54	2.95
308.15	0.123	0.693	1.36	1.94	2.42	2.80
313.15	0.118	0.664	1.31	1.86	2.32	2.68
318.15	0.114	0.639	1.26	1.79	2.23	2.58
323.15	0.110	0.619	1.22	1.73	2.16	2.50
328.15	0.107	0.603	1.19	1.69	2.10	2.44
333.15	0.105	0.591	1.16	1.65	2.06	2.39
338.15	0.103	0.581	1.14	1.63	2.03	2.35
343.15	0.102	0.574	1.13	1.61	2.00	2.32

by Wilcock and Battino[176] who showed that within their experimental error of $\pm 1\%$ that a mixture of 49.5 mol % oxygen + 50.5 mol % nitrogen gave the same results as those calculated for solubilities of the pure gases. So, at least to 1% at atmospheric pressure, air solubilities may be calculated from the knowledge of nitrogen (78.1%), oxygen (21.0%), and argon (0.9%) solubilities in the liquid. For greater precision, direct measurements must be carried out.

In this section, we will discuss the solubility of air in various liquids. A more complete coverage may be found in Ref. 1.

5.1. Water and Aqueous Salt Solutions

Winkler[177] calculated the values of air solubilities in water from his results with nitrogen and oxygen. These values should be a fair approximation to directly measured ones and are presented for general use in Table 58. The following equation fits Winkler's data with a standard deviation of

Table 60. Ostwald coefficients for air solubilities in hydrocarbons and oxygen containing solvents

Solvent	T/K	Ostwald coefficient
n-Heptane	298.15	0.245 [68]
n-Octane	298.15	0.226 [68]
2,2,4-Trimethylpentane	293.15	0.258 [70]
	298.15	0.247 [68]
n-Decane	298.15	0.180 [68]
1-Heptane	298.15	0.121 [68]
1-Octanol	298.15	0.118 [68]
Diethyl ether	273.15	0.290 [40]
	283.15	0.287 [40]
	288.15	0.286 [40]

Table 61. Mole fraction solubilities for air in n-dodecane

at total pressures indicated [113]

T/K	P/MPa	x_1
248.82	1.03	0.0142
373.15	1.03	0.0161
297.40	2.07	0.0312
373.15	2.07	0.0330
297.65	4.82	0.0722
373.15	4.82	0.0768
297.15	10.34	0.1491
373.15	10.34	0.1579

0.0016 in ln x_1. This corresponds to about 0.24% in x_1.

$$\ln x_1 = -104.208 + 137.296/\tau$$
$$+ 58.7394 \ln \tau - 5.7669 \tau. \quad (108)$$

A modern value by Baldwin and Daniel[70] also appears in Table 58 and is in agreement with Winkler's value within the precision of the fit.

McKee[178] and Eichelberger[179] both measured the solubility of air in water at pressures above atmospheric. For McKee, it was 273–295 K and 3.5–20.7 MPa and for Eichelberger it was 298–338 K and 6.8–24.2 MPa. The following equation fits the data as S [cm^3 (STP) per gram of water] in the combined ranges:

$$\ln S = -46.031 + 68.471/\tau + 19.316 \ln \tau$$
$$- 0.020\ 613(P/\text{MPa}) + 1.1243 \ln(P/\text{MPa}),$$
$$(109)$$

Table 62. Ostwald coefficient solubilities for air solubilities

in a variety of halogen containing compounds at 298.15 K

Solvent	Ostwald Coefficient, L
1-Bromoheptane	0.132 [68]
1-Bromo-1,1,2,2,3,3,4,4,5,6,6,6-dodecafluoro-5-(trifluoromethyl)hexane	0.360 [181]
1-Chloro-1,1,2,2,3,3,4,4,5,6,6,6-dodecafluoro-5-(trifluoromethyl)hexane	0.374 [181]
1-Bromo-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane	0.341 [181]
Octadecafluorooctane; (perfluorooctane)	0.374 [181]
Octadecafluorodecahydronaphthalene; (perfluorodecalin)	0.298 [181]
1,1,1,2,4,4,5,7,7,8,10,10,11,13,13,14,16,16,17,17-18,18,18-Tricosafluoro-5,8,11,14-tetrakis(trifluoromethyl)-3,6,9,12,15-pentaoxaoctadecane	0.318 [181]
L1822	0.320 [181]
FC75	0.377 [181]
1,1,2,2,3,3,4,4,-Nonafluoro-N,N-bis(nonafluorobutyl)-1-butanamine; (perfluorotributylamine)	0.307 [181]

with a standard deviation of 0.020 in ln S. Smoothed values are presented in Table 59.

Eichelberger[179] measured the solubility of air in aqueous NaCl solutions in the range $T = 298$–338 K, $p = 7.0$–24.2 MPa, $\rho_{\text{NaCl}} = 0$–309 g/L. Kobe and Kenton[180] determined the solubility of air and air/CO$_2$ mixtures in aqueous solutions of sulfuric acid and sodium sulfate at 298 K and 101 kPa.

5.2. Hydrocarbons and Oxygen Containing Solvents

Table 60 gives the Ostwald coefficients for air solubilities in a number of hydrocarbon solvents and oxygen containing solvents.

Table 61 gives pressure and temperature dependent data[113] for air solubilities in n-dodecane.

5.3. Halogen Containing Solvents

In Table 62, we present Ostwald coefficient solubilities for air in a variety of halogen containing solvents. The precision of these measurements is 2%–5%.

5.4. Miscellaneous

Ref. 1 contains data for miscellaneous animal and vegetable oils, lubricating oils, mineral oils, and various fuels.
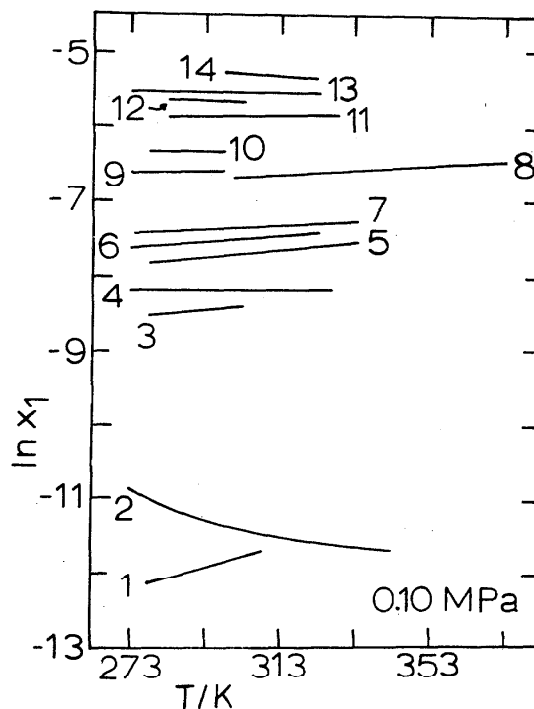

FIG. 7. Some representative mole fraction solubilities of nitrogen at 0.101 325 MPa. 1—hydrazine; 2—water; 3—carbon disulfide, 4—methanol; 5—benzene, 6—acetone; 7—carbon tetrachloride; 8—n-hexadecane; 9—n-hexane; 10—hexafluorobenzene; 11—olive oil; 12—perfluorotributylamine, 13—perfluoro-n-heptane, 14—1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl) ethoxy]-hexane or perfluoro-1-isopropoxy hexane or caroxin-F.

6. Conclusions

Nitrogen is the most common gas in our atmosphere and as such its solubility has been determined in a large variety of fluids and over a considerable range of temperature and pressure. In this article, we have attempted a critical evaluation of the solubility data in the literature, summarizing it in many tables and smoothing equations. We provided smoothing equations for both temperature and pressure combined. In the case of the *n*-alkanes and the 1-alkanols, we also provided smoothing equations in terms of carbon number. An examination of the information in this paper reveals some gaps in the literature and some systems that need more definitive study. Since we limited this paper to a critical evaluation of solubility data we have made no reference to theories relating to the solubility of gases. References 3, 4, 6, 15, and 16 may be of some use in this regard. Finally, for perspective, we present in Fig. 7 a graph of some representative solubilities of nitrogen at 0.101 325 MPa as a function of temperature.

7. Acknowledgments

8. References

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