Solubility of Nitrogen, Argon, Methane, and Ethane in Ethylene Oxide

James D. Olson

Research and Development Department, Chemicals and Plastics, Union Carbide Corporation, South Charleston, West Virginia 25303

Henry's constants for nitrogen, argon, methane, and ethane in ethylene oxide (75-21-8) were measured over a pressure range of 2-22 atm at 0, 25, and 50 °C. An experimental technique was developed in which the gas solubility is calculated from a material balance after measurement of the equilibrium pressure of the undissolved gas above a gravimetrically prepared sample of the mixture which is confined in a closed bomb of known volume. The Henry's constants (mole fraction) at 25 °C are N_2 2180 atm, Ar 1420 atm, CH_4 614 atm, and C_2H_6 109 atm. Between 0 and 50 °C, the Henry's constant of methane is nearly temperature independent while the Henry's constant of ethane increases with increasing temperature. Nitrogen and argon Henry's constants decrease with increasing temperature.

Data on gas solubility in ethylene oxide, an important starting material in the production of industrial chemicals, are important for the efficient design and operation of chemical reactors and separation units. There are no reported experimental data for nonpolar gases dissolved in ethylene oxide, although some solubilities were given in a table by Hess and Tilton (5). The values implied for nitrogen in that article are in error. The purpose of the present article is to report experimental gas solubilities in the form of Henry's constants at 0, 25, and 50 °C for nitrogen, argon, methane, and ethane in ethylene oxide.

The method of gas solubility measurement employed here depends on a material balance for a closed bomb, rather than direct sampling and analysis of the liquid phase. The novel feature of our procedure is that a 5-kg two-pan analytical balance, which has resolution of 1 mg, is used to accurately measure the total amounts of gas and liquid confined in a previously evacuated bomb of known total volume. This contrasts with typical previously reported material balance experiments (2, 11) where total amounts were deduced from volumetric measurements and a knowledge of the equation of state behavior of the gas. The gravimetric gas solubility method is advantageous for measurements on solvents whose ambient vapor pressure exceeds 1 atm because a glass apparatus is not required.

The data are obtained by carefully weighing the addition of an amount of degassed liquid to an evacuated sample bomb, adding a precisely weighed sample of gas, and then measuring the final pressure of the gas after alternately shaking the bomb and allowing it to stand in a constant temperature bath.

Experimental Section

A sample of UCC commercial grade ethylene oxide was used without further purification other than degassing. Analysis of the sample by gas chromatography revealed no volatile impurities above the level of 100 ppm. Matheson research grade methane (99.99%) and ethane (99.96%) were used except for the last few methane experiments which were performed with Linde CP (99.0%). Linde High Purity (99.99%) nitrogen and Ultra-High Purity (99.999%) argon were used. These purities are well above the 99 mole % minimum usually required for gas solubility experiments (1).

The gas solubility bomb was constructed from a stainless steel Hoke sampling cylinder (volume $\approx$350 cm³) fitted with valves

used to isolate the pressure gauge from the pressure bomb during shaking and handling. Several stainless steel balls were added to the bomb before assembly to ensure thorough mixing upon shaking. A Marsh Instrument Company Master Test (0.25%) bourdon gauge was attached to the top of the bomb. Three bombs were assembled with three gauges, 0-200, 0-400, 0-600 psia. The accuracy and the repeatability of the pressure gauges were checked against a newly calibrated 0-500 psia Heise gauge which has 0.1% accuracy traceable to NBS. In addition, ethylene oxide vapor pressures were measured at 50 °C. The total volume of each assembled bomb was calculated with a precision of ±0.1% from the virial equation of state after measurement of the weight of the bomb filled with nitrogen.

A 5-kg Voland two-pan analytical balance was used to weigh the sample bomb directly before and after addition of each component. The balance was used with class S weights and an electronic device which reads out to 1 mg between the integer gram reading. The milligram readout device was checked with a set of 1-500-mg weights. All weighings were corrected for air buoyancy. The use of this high precision balance is the most important experimental feature of the gravimetric gas solubility procedure.

The sample bombs were equilibrated to ±0.1° in three different thermostats, at 0, 25, and 50 °C. The ±0.1° temperature control is usually sufficient for a gas solubility experiment (1). In all three thermostats, the absolute temperature was measured with mercury-in-glass thermometers that had been checked against a Leeds and Northrup primary standard platinum resistance thermometer.

The experimental procedure was as follows: The previously evacuated and weighed sample bomb was filled about 60% full of ethylene oxide which had been degassed by boiling at atmospheric pressure. The bomb was placed in an acetone-ice bath during the filling process to lower the vapor pressure of the ethylene oxide in the bomb. After equilibration at room temperature and after thorough drying, the bomb was reweighed, filled with the sample gas to an appropriate pressure, and immediately reweighed. The bomb was then placed in a thermostat and equilibrated. Usually 2-4 h were required to obtain a stable pressure reading at which time the bomb could be placed in a different thermostat to obtain data at another temperature. The bomb was then emptied, dried, and placed on the vacuum system to be pumped out overnight before the next experiment.

Data Reduction

The following quantities are measured during an experimental run: (1) the volume of the bomb, measured in a separate calibration experiment; (2) total mass of liquid solvent added to the evacuated pressure vessel; (3) total mass of gas added to the pressure vessel after addition of the liquid; (4) equilibrium pressure of the mixture at a particular temperature. From these experimental data, the amount of gas dissolved in the liquid can be calculated from a material balance on the amount of gas that remains in the vapor phase. This is accomplished by simultaneous solution of the equations of thermodynamic phase equilibrium and the equation of state for the vapor-phase mixture.

The technique of data reduction employed here is similar to the treatment described by Cukor and Prausnitz (2) with the addition of: (i) an equation for the vapor volume that contains a

Table I. Physical Properies of Ethylene Oxide

	T (°C)		
	0	25	50
Sat. liquid density (g cm^{-3})	0.8969	0.8627	0.8265
Sat. vapor density (g cm^{-3})	0.00132	0.00337	0.00724
Vapor pressure (atm)	0.650	1.725	3.879
C_{11}, cohesive energy density (cal cm^{-3})[a]	110.20	94.02	80.49
B_{11} (cm^3 g-mol^{-1})[b]	−998.0	−722.0	−551.9

[a] Used in $\bar{V}_2^\infty$ correlation, ref 6. [b] Estimated from correlation, ref 10.

Table II. Volumetric Properties of Gases

		cm^3 g-mol^{-1}			
	T (°C)	N_2	Ar	CH_4	C_2H_6
B_{22}[a]	0	−10.27	−21.45	−53.61	−223.0
	25	−4.71	−15.76	−42.84	−187.0
	50	−0.28	−11.24	−34.15	−157.0
B_{12}[b]	0	−85.9	−119.1	−160.4	−331.2
	25	−69.4	−98.6	−133.3	−273.0
	50	−56.2	−82.3	−111.9	−229.2
$\bar{V}_2^{\alpha}$ [c]	0	41.1	35.9	44.4	61.3
	25	43.3	39.5	47.5	64.5
	50	48.5	43.6	52.0	68.6

[a] Experimental data, ref 4. [b] Estimated from correlation, ref 10. [c] Estimated from correlation, ref 6.

Table III. Experimental Henry's Constants (atm/mole fraction)

T (°C)	N_2	Ar	CH_4	C_2H_6
0	2800	1670	613	84.3
25	2180	1420	614	109
50	1820	1270	595	129

Table IV. Experimental Conditions

		T (°C)		
		0	25	50
N_2	NOPT[a]	6	11	3
	$\hat{\sigma}_H$[b]	2.9%	3.3%	2.4%
	P[c]	7–20	9–22	18–21
	$100X_2$[d]	0.2–0.7	0.3–0.9	0.7–0.9
Ar	NOPT	8	8	3
	$\hat{\sigma}_H$	3.1%	1.0%	0.2%
	P	5–17	7–21	14–17
	$100X_2$	0.3–1.1	0.3–1.3	0.7–0.9
CH_4	NOPT	8	8	4
	$\hat{\sigma}_H$	3.2%	2.5%	1.4%
	P	6–18	8–20	12–20
	$100X_2$	0.8–2.7	0.9–2.9	1.2–2.5
C_2H_6	NOPT	6	6	4
	$\hat{\sigma}_H$	3.2%	2.9%	0.5%
	P	2–3	3–5	8.0–8.3
	$100X_2$	1.6–3.1	1.5–3.0	3.0–3.2

[a] NOPT number of experimental runs. [b] $\hat{\sigma}_H$, experimental standard deviation (RMS error % of $\hat{H}$). [c] P, experimental pressure range, atm. [d] $100X_2$, experimental dissolved gas range, mole %.

correction for the liquid-phase expansion after gas takeup and (ii) pressure corrections to the reference fugacity of each component. In both cases, the correction is necessary because of the magnitude of the experimental pressures (2–22 atm).

The number of moles of gas dissolved in the liquid at equilibrium is related by a material balance to the total moles of gas added and the number of moles of gas remaining in the vapor phase,

$$n_2^L = n_2^T - n_2^V \tag{1}$$

so that the liquid-phase mole fraction is,

$$x_2 = (n_2^T - n_2^V)/(n_1^T + n_2^T - n_1^V - n_2^V) \tag{2}$$

The gas solubility is characterized by Henry's constant H defined as,

$$H = \lim_{x_2 \to 0} (f_2/x_2) \tag{3}$$

where f_2 is the fugacity.

The equations which describe thermodynamic equilibrium between the phases at a particular temperature T and equilibrium pressure P are,

$$\phi_1 y_1 P = x_1 P_1^{sat} \phi_1^{sat} \exp[(P - P_1^{sat})V_1/RT] \tag{4}$$

for the solvent and,

$$\phi_2 y_2 P = x_2 H \exp[(P - P_1^{sat})\bar{V}_2^\infty/RT] \tag{5}$$

for the solute (gaseous component), where ϕ is the vapor-phase fugacity coefficient, y is the vapor-phase mole fraction, P_1^{sat} is the pure solvent saturated vapor pressure, V_1 is the pure solvent saturated molar volume, and $\bar{V}_2^\infty$ is the partial molar volume of the gas dissolved in the liquid at infinite dilution. The exponential pressure correction terms contain usual approximations (8) for the pressure dependence of the volumetric properties of the liquid phase. Equation 5 is often called the Krichevsky–Kasarnovsky equation (9) or the "pressure-corrected" Henry's law.

The equation of state employed here to describe the volumetric properties of the vapor-phase mixture is the virial equation truncated after the first density correction,

$$P/\rho RT = 1 + B_M \rho \tag{6}$$

$$\rho = (n_1^V + n_2^V)/V^V \tag{7}$$

$$B_M = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{8}$$

where B_{11}, B_{22}, and B_{12} are the pure component and mixed second virial coefficients. In addition, the vapor-phase fugacity coefficients can be calculated from the second virial equation,

$$\ln \phi_1 = 2\rho[y_1 B_{11} + y_2 B_{12}] - \ln (P/\rho RT) \tag{9}$$

$$\ln \phi_2 = 2\rho[y_2 B_{22} + y_1 B_{12}] - \ln (P/\rho RT) \tag{10}$$

The vapor volume, V^V, was calculated from the total volume and the volume occupied by the liquid phase at equilibrium,

$$V^V = V^T - [(n_1^L V_1 + n_2^L \bar{V}_2^\infty)(1 - \alpha P)] \tag{11}$$

where α is the isothermal compressibility of the liquid phase, negligible at our experimental pressures ($\alpha \simeq 10^{-4}$ atm^{-1}).

Gas solubilities were calculated from the iterative simultaneous solution of eq 2, 4, 5, 6, 9, 10, and 11. Convergence was assumed when the same values of n_1^V and n_2^V satisfied all the equations. A FØRTRAN computer routine was written which typically converged after two–four iterations and which gave the Henry's constant corrected to zero partial pressure of gas as indicated by eq 3 and 5. Computational details are available from the author.

The physical property data used for the ethylene oxide gas solubility calculations are listed in Tables I and II. Some of the quantities were estimated from correlations as indicated. Of particular importance for the data reduction were the Tsonopoulos virial coefficient correlation (10) and the correlation of Lyckman et al. (6) for infinite dilution partial molar volume of gas dissolved in the liquid.

Before carrying out the ethylene oxide experiments, a test experiment on the system nitrogen in cyclohexane at 25 °C and

Table V. Comparison of Henry's Constants, atm

Gas	T (°C)	Ref 5	This work[a]
N_2	30	630	2087
	45	630	1871
CH_4	30	610	612
	45	610	600
C_2H_6	30	96	113
	45	112	125

[a] Interpolated from 0, 25, and 50 °C results.

pressures between 7 and 24 atm produced the following result: H (atm) 1302.1, ref 3; 1286.0, this work; $\Delta = 1.24\%$. If a slightly lower V_2^∞ is used (42 instead of 49 cm³ g-mol⁻¹), exact agreement with the literature value is obtained.

Results

Results for 75 gravimetric experiments on the solubility of nitrogen argon, methane, and ethane in ethylene oxide are shown in Table III. The Henry's constants are mean values calculated from the number of replicate experiments indicated in Table IV for each temperature. Also tabulated in Table IV are the pressure ranges and calculated liquid mole fractions ranges which define the experimental conditions for which the validity of eq 4, 5, and 6 is claimed.

No statistically significant dependence of H on bomb used, chronological order of experiments, pressure range, or other environmental factors could be detected. Hence, each experimental value was given equal weight in the calculation of the average values $\hat{H}$.

The precision of the results is indicated by the estimated standard deviation, $\hat{\sigma}_H$, of each of the Henry's constants. $\hat{\sigma}_H$ is the root-mean-square error expressed as a percentage of the particular Henry's constant. Their values range from $0.2\% \leq (\hat{\sigma}_H) \leq 3.3\%$ for experiments on four different gases at three different temperatures. An overall relative precision estimate was calculated,

$$\langle \hat{\sigma}_H \rangle = 2.4\%$$

On this basis the precision of the procedure was 1–3% depending on the particular system and the temperature.

The evaluation of the accuracy of experimental measurements in the absence of exactly known reference values is a difficult and ill-defined process (7). If no systematic errors (bias) exist, the experimental uncertainty is the same as the uncertainty expected from random errors, 1–3%, as indicated by the precision estimate. The rehearsal experiment on a previously studied system, nitrogen in cyclohexane, indicates that serious systematic errors are absent from the procedure. However, the accuracy of the gravimetric gas solubility procedure is ultimately determined by the validity of eq 4, 5, and 6 and by the applicability of the correlations (6, 10) used in the data reduction.

The use of eq 4 and 5 (without activity coefficients) is valid for a sparingly soluble gas at conditions remote from critical (9). For example, in the case of nitrogen dissolved in water, eq 5 is valid to pressure of 1000 atm. However, the pressure range over which the "pressure-corrected" Henry's law is valid depends on (i) the concentration of gas dissolved in the liquid phase and (ii) the chemical similarity of the particular gas–liquid pair. If, for either reason, solute–solvent interactions become significant, deviations from eq 5 may occur; these deviations can be characterized by an "unsymmetric" activity coefficient (9). During the ethylene oxide experiments, the liquid-phase solution was sufficiently dilute (less than 3 mole % gas) so that eq 5 can be assumed to be valid. See Table IV.

The magnitude of error introduced into the Henry's constant from uncertainties in the estimated value of V_2^∞ is about 1% in H for a 10% change in V_2^∞. The effect of errors propagated
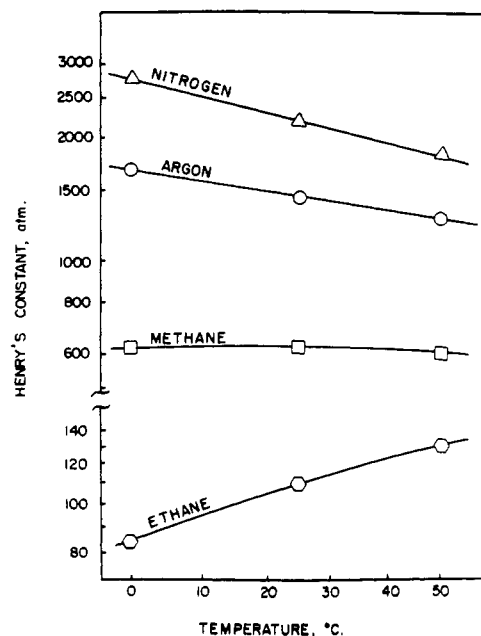

Figure 1. Henry's constants in ethylene oxide.

from the estimated virial coefficients, B_{11} and B_{12}, is even less; for example, the calculated value of $\hat{H}$ for the 25 °C argon data increased about 0.2% for a 35% increase in B_{11} combined with a 10% increase in B_{12}. This is because the mixture virial coefficient is most sensitive to B_{22} due to the large vapor-phase mole fraction of the light component. The values of B_{22} used were taken from experimental data compiled by Dymond and Smith (4).

Table V is a comparison of Henry's constants from this work with the results published earlier (5). The methane results are in agreement while the ethane results differ by about 16%, probably because of the nonideality of ethane near its critical point. The nitrogen results, however, disagree by more than 300%.

The temperature dependence of the Henry's constants is shown in Figure 1 which is a ln H vs. $1/T$ plot. These temperature trends are consistent with theory (9). At temperatures just above the critical point of the gas, solubility is expected to decrease with increasing temperature while at temperatures well above the gas critical temperature, gas solubility tends to increase with increasing temperature. Therefore, at some intermediate temperature, there must be a "reversal" of the temperature dependence. Figure 1 indicates that the more supercritical gases, nitrogen and argon, are well above their reversal temperatures while ethane, whose critical temperature is 32 °C, is well below its reversal temperature. The fourth gas, methane, has an intermediate critical point and, consequently, its solubility shows only slight temperature dependence which suggests methane is in the vicinity of its reversal temperature.

Acknowledgments

Glossary

B_{ij}	second virial coefficient, interaction between molecules i and j, cm³ g-mol⁻¹
B_M	mixture second virial coefficient, cm³ g-mol⁻¹
C_{11}	cohesive energy density of liquid solvent, cal cm⁻³

f_i	fugacity of component i, atm
H	Henry's constant, atm
$\hat{H}$	mean of experimental Henry's constants, atm
n_i	moles of component i
P	pressure, atm
P_i	partial pressure of component i, $y_i P$, atm
R	gas constant, 82.056 cm^3 atm K^{-1} g-mol^{-1}
T	absolute temperature, K
V^i	volume of phase i, cm^3
V_1	saturated liquid molar volume of solvent, cm^3 g-mol^{-1}
$\overline{V_i}$	partial molar volume of component i, cm^3 g-mol^{-1}
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i

Greek

α	isothermal compressibility of liquid phase, $-(1/V)(\partial V/\partial P)_T$, atm^{-1}
ρ	molar density, g-mol cm^{-3}
$\hat{\sigma}_H$	standard root-mean-square error of experimental Henry's constant
ϕ_i	fugacity coefficient of component i

Subscripts

1	of the solvent (liquid)
2	of the solute (gas)
M	of the mixture

Superscripts

T	total in system (added to bomb)
L	in the liquid phase
V	in the vapor phase
sat	pure saturated solvent, component 1
∞	at infinite dilution

Literature Cited

(1) Clever, H. L., Battino, R., "Techniques of Chemistry, Vol. VIII, Part I, Solutions and Solubilities", M. R. J. Dack, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter VII.
(2) Cukor, P. M., Prausnitz, J. M., *J. Phys. Chem.*, **76**, 598 (1972).
(3) Dymond, J. H., Hildebrand, J. H., *Ind. Eng. Chem., Fundam.*, **6**, 130 (1967).
(4) Dymond, J. H., Smith, E. B. "The Virial Coefficients of Gases", Clarendon Press, Oxford, 1969.
(5) Hess, L. G., Tilton, V. V., *Ind. Eng. Chem.*, **42**, 1251 (1950).
(6) Lyckman, E., Eckert, C. A., Prausnitz, J. M., *Chem. Eng. Sci.*, **20**, 685 (1965).
(7) Mandel, J., "The Statistical Analysis of Experimental Data", Interscience, New York, N.Y., 1964, p 125.
(8) Prausnitz, J. M., Eckert, C. A., Orye, R. A., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1967, pp 12–26.
(9) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1969, Chapter 8.
(10) Tsonopoulos, C., *AIChE J.*, **20**, 263 (1974).
(11) Volk, H., Halsey, G. D., Jr., *J. Chem. Phys.*, **33**, 1132 (1960).

Densities of the Molten Salt System Cesium Bromide–Cuprous Bromide

Gert J. Lamprecht
Department of Chemistry, University of Zululand, Kwa-Dlangezwa 3886, Republic of South Africa

Densities of the molten salt system cesium bromide–cuprous bromide have been measured at nine mole fractions over the complete composition range and in the temperature range 507–950 °C using the method of Archimedean displacement. The temperature coefficients of the densities have been evaluated from these measurements.

The present work was undertaken as part of a research project of the above mentioned department on the properties of molten cuprous halide–alkali halide systems.

Experimental Section

Materials. Cesium bromide (Merck/Suprapur) was dried under dynamic vacuum at 300 °C for 24 h and used without further purification. Cuprous bromide (Riedel-de Haën, 99%) was further purified (*4, 5*) by dissolving it in the minimum amount of 47% hydrobromic acid (Merck/Suprapur) and reprecipitating by dilution with deaerated distilled water containing 1 g of anhydrous sodium sulfite per liter. The white precipitate was washed successively with water (as described for the dilution process) and acetone and then vacuum dried as specified for the cesium bromide. To minimize oxidation of the purified cuprous bromide during subsequent handling it was melted under vacuum and formed a light green crystalline substance upon cooling. All storage and handling of the purified salts took place under an atmosphere of nitrogen, purified and dried by passing it through columns containing silica gel (Merck) and Type 5A molecular sieve (BDH Chemicals Limited).

Apparatus and Procedure. The furnace, balance, sample assembly, and experimental procedure were similar to those described by Brookes and Paul (*1*), except for the following respects.

The nichrome suspension wire hanging from the stirrup of the balance to the sinker (bob) went through a short length (2 cm) of a Silicone rubber tube attached to the top of the Pyrex tube enclosing the suspension wire. The Silicone tube could be clamped vacuum tight which enabled the system to be evacuated or kept under a completely closed inert atmosphere. During the short time an actual mass measurement was conducted the clamp on the Silicone tube was released and dry purified nitrogen escaped through the Silicone tube to the atmosphere. The nitrogen was released at a fixed pressure during each mass measurement to ensure a constant upthrust by the gas on the suspension wire. Prior to each mass measurement the system was subjected to a vacuum to remove possible nitrogen bubbles from the sinker.

The relatively high vapor pressure of cuprous bromide (*3*) leads to condensation on the suspension wire. To correct for the condensation the wetting of the sinker, after immersion in a molten salt mixture, was determined at the beginning of each run before condensation occurred on the suspension wire. The wetting of the sinker as a function of temperature at a given mole fraction was determined by duplicate runs beginning at various temperatures. Once the wetting of the sinker was known it was possible to make a correction for the condensation on the sus-