

ESTIMATION OF HENRY'S CONSTANTS FROM HIGH PRESSURE GAS SOLUBILITIES. THE SYSTEMS CO₂ + n-HEXANE AND N₂O + n-HEXANE

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abstract: Experimental determination of gas solubilities of CO₂ and N₂O in n-hexane (at pressures up to 50 bar and temperatures 0, 5, 10, 15 and 25°C) will be presented. Henry's constants will be estimated by using of Krichevsky-Kazarnovsky and Krichevsky-Ilinskaya equations.

Introduction

The solubility of gases in liquids is an area of active interest from both the theoretical and practical standpoints. Both the dilute solutions resulting from the low solubility of many gases in liquids, and the large variety of sizes, shapes and polarities of gas molecules to act as "probes" have made the solubility of gases in liquids an excellent tool to investigate the test theories of liquid properties and liquid structure. A knowledge of the solubility of gases is of practical importance in various industrial processes, in the study of artificial atmospheres for divers and astronauts, in the interaction of gases with our environment, in processes for saline water demineralization, and in the study of various biological fluids and tissues [1].

This paper deals with experimental determination of gas solubilities of CO₂ and N₂O in n-hexane (at pressures up to 50 bar and temperatures 0, 5, 10, 15 and 25°C) and from these values we have calculate the Henry's constants by using of Krichevsky-Kazarnovsky and Krichevsky-Ilinskaya equations.

Theoretical considerations

From theoretical point of view, problem of gas solubility in liquids represents a particular case of liquid – vapor phase equilibrium.

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$$(C_1 + C_2)^l \Leftrightarrow C_2^g \quad (1)$$

The general relation which governs this process derive from general condition of thermodynamic equilibrium, namely:

$$\mu_2^l = \mu_2^g, \text{ or } f_2^l = f_2^g \quad (2)$$

By introduction of significance of solute fugacity in both phases we obtain:

$$f_2^{0,l} \cdot \gamma_2^l \cdot x_2^l = x_2^g \cdot \gamma_2^g \cdot P \quad (3)$$

that represents generalised form of Raoult's law. Because Henry's law shows the proportionality between gas fugacity and its concentration in the solution,

$$f_2^g = H \cdot x_2^l \quad (4)$$

results that the product $f_2^{0,l} \cdot \gamma_2^l$ represent just the Henry's constant (which depends on the nature of both components – depends on the nature of solvent by means of activity coefficient γ_2^l). The Henry's constant depends only on the temperature.

Taking as standard state the ideal dilute solution, even by definition of Henry's constant, it means that for a concentrate solution (at high pressures) the equation (4) should be corrected by introduction of the activity coefficient in asymmetric convention, γ_2^{*l} :

$$\begin{aligned} \gamma_1^l &\rightarrow 1 \quad \text{when } x_1^l \rightarrow 1 \quad \text{for solvent and} \\ \gamma_2^{*l} &\rightarrow 1 \quad \text{when } x_2^l \rightarrow 0 \quad \text{for solute} \end{aligned}$$

Introduction of asymmetric convention of normalization eliminates the arbitrary in the definition of $f_2^{0,l}$ (standard state fugacity of solute), which can be experimentally determinate:

$$f_2^{0,l} = \lim_{x_2^l \rightarrow 0} \left(\frac{f_2^g}{x_2^l} \right) = H_{2,1}^{P_1^s} \quad (5)$$

where $H_{2,1}^{P_1^s}$ represents the Henry's constant for solute 2 in solvent 1 at the system temperature and the P_1^s (the saturation pressure of pure solvent).

As long as the pressure is not large, the pressure dependence of Henry's constant can be neglected. At high pressure the effect is not negligible and therefore it is necessary to consider how Henry's constant depends on pressure. This dependence is obtain by using the equation:

$$\left(\frac{\partial \ln f_2^l}{\partial P} \right)_{T, x_2^l} = \frac{\bar{V}_2^l}{RT} \quad (6)$$

where \bar{V}_2^l is the partial molar volume of solute in the liquid phase. By substitution of relation (5) in equation (6) we finally obtain:

$$\ln \frac{f_2^g}{x_2^l} = \ln H_{2,1}^{P_1^s} + \frac{\bar{V}_2^{\infty,l} \cdot (P - P_1^s)}{RT} \quad (7)$$

where we assume that the partial molar volume at infinite dilution, $\bar{V}_2^{\infty,l}$, is independent on pressure. The above equation is known as *Krichevsky-Kasarnovsky equation*. This equation is very useful for representing solubilities of sparingly soluble gases to very high pressures.

In more cases is not reasonable to expect that the activity coefficient of the solute in the liquid phase is independent of composition or that the partial molar volume is constant. Variation of the activity coefficient of the solute with the mole fraction can be given by two-suffix Margules equation:

$$\ln \gamma_1^l = \frac{A}{RT} \cdot (x_2^l)^2 \quad (8)$$

where A is an empirical constant determined by intermolecular forces in the solution.

The activity coefficient γ_2^{*l} of the solute normalized according to the unsymmetric convention is found from the Gibbs-Duhem equation:

$$\ln \gamma_2^{*l} = \frac{A}{RT} \cdot [(x_1^l)^2 - 1] \quad (9)$$

The fugacity of component 2 at pressure P_1^s is:

$$f_2^l = \gamma_2^{*l} \cdot H_{2,1}^{P_1^s} \cdot x_2^l \quad (10)$$

Instead of equation (7) we obtain:

$$\ln \frac{f_2^g}{x_2^l} = \ln H_{2,1}^{P_1^s} + \frac{A}{RT} \cdot [(x_1^l)^2 - 1] + \frac{\bar{V}_2^{\infty,l} \cdot (P - P_1^s)}{RT} \quad (11)$$

Equation (11) is known as *Krichevsky-Ilinskaya equation*.

For liquid-gas solutions, Krichevsky-Ilinskaya equation represents a significant improvement with regard of Krichevsky-Kasarnovsky equation. Between the three parameters of the equation, the Henry's constant is the most important. Henry's constant has always positive values while A and $\bar{V}_2^{\infty,l}$ can be positive or negative [2-9].

Materials and method

Principle of experimental method as well as working procedure and analysis of obtained data were presented in a previous work [10].

N-hexane was a Merck Schuchardt solvent zur Synthese (d at 20°C is 0.659), carbon dioxide was a pure Linde gas (99.9%) and N₂O was for medical use.

Experimental parameters were measured with high precision (working pressure ± 0.01 bar, working temperature ± 0.02°C, pressure of desorbed gas ± 0.05 mm Hg, and mass of solvent- with analytical balance).

Results and Discussions

Tables 1 and 2 contain the Henry's constants calculated from both methods (Krichevsky-Kazarnovsky and Krichevsky-Ilinskaya equations). These data were obtained by using of experimental solubilities values of CO₂ and N₂O in n-hexane at various temperatures and pressures [11]. The gas fugacities at different temperatures and pressures were calculated by using of computing programme based on Redlich-Kwong equation:

$$\ln f = \ln \frac{RT}{V-b} + \frac{a}{bRT^{3/2}} \ln \frac{V}{V+b} + \frac{b}{V-b} - \frac{a}{RT^{3/2}(V+b)}$$

where $a = 0.42748 \cdot R^2 \cdot \frac{T_c^2}{P_c}$ and $b = 0.08664 \cdot R \cdot \frac{T_c}{P_c}$.

For CO₂: T_c = 304.1 K and P_c = 73.8 atm.

For N₂O: T_c = 309.6 K and P_c = 72.4 atm.

Because experimental measurements were performed at high pressures, the vapor pressure of pure solvent, P₁^s, can be neglected.

Table 1 Calculated data for the system CO₂ + n-hexane

T [K]	P [bar]	x ₂ ^l	f ₂ ^g	ln $\frac{f_2^g}{x_2^l}$	ln $\frac{f_2^g}{x_2^l} - \frac{\bar{V}_2^\infty}{RT} \cdot (P - P_1^s)$	H _{2,1}	
						K-K (eq. 7)	K-I (eq. 11)
273.15	37.43	0.450	28.78	4.16	4.07	108.10	105.15
	36.26	0.380	28.15	4.31	4.22		
	32.04	0.365	25.72	4.26	4.18		
	30.38	0.331	24.69	4.31	4.24		
	24.85	0.219	18.90	4.46	4.40		
	20.58	0.204	17.96	4.48	4.27		
	12.74	0.122	11.73	4.56	4.53		
	5.68	0.058	5.48	4.55	4.54		

278.15	44.00	0.508	32.63	4.16	4.06	127.89	126.43
	39.00	0.421	30.11	4.27	4.17		
	29.10	0.281	24.15	4.45	4.38		
	21.46	0.194	18.76	4.57	4.52		
	8.13	0.071	7.74	4.69	4.67		
283.15	41.45	0.379	31.92	4.43	4.33	144.98	144.34
	41.25	0.368	31.82	4.46	4.36		
	30.96	0.260	25.64	4.59	4.52		
	21.75	0.176	19.12	4.69	4.64		
	12.54	0.094	11.66	4.82	4.79		
288.15	44.78	0.351	34.23	4.58	4.47	149.04	150.14
	41.25	0.340	32.30	4.55	4.46		
	33.51	0.254	27.59	4.69	4.61		
	30.87	0.222	25.85	4.76	4.69		
	21.75	0.152	19.24	4.84	4.79		
298.15	9.99	0.073	9.46	4.86	4.84	158.35	160.77
	52.33	0.350	39.33	4.72	4.60		
	41.65	0.265	33.40	4.84	4.74		
	41.35	0.261	33.22	4.85	4.75		
	31.85	0.203	27.01	4.89	4.82		
	31.65	0.201	26.87	4.90	4.83		
	26.75	0.169	23.32	4.93	4.87		
	15.68	0.100	14.49	4.98	4.94		
	11.85	0.081	11.17	4.93	4.90		
7.05	0.046	6.81	4.99	4.98			

Table 2 Calculated data for the system N₂O + n-hexane

T [K]	P [bar]	x_2^l	f_2^g	$\ln \frac{f_2^g}{x_2^l}$	$\ln \frac{f_2^g}{x_2^l} - \frac{\bar{V}_2^\infty}{RT} \cdot (P - P_1^s)$	$H_{2,1}$	
						K-K (eq. 7)	K-I (eq. 11)
273.15	29.60	0.486	24.20	3.91	3.84	74.40	76.05
	24.79	0.351	21.00	4.09	4.03		
	19.70	0.275	17.30	4.14	4.09		
	15.20	0.212	13.77	4.17	4.13		
	9.70	0.154	9.12	4.14	4.12		
	6.08	0.084	5.85	4.24	4.23		
278.15	30.90	0.393	25.32	4.17	4.09	84.54	81.28
	24.60	0.309	21.06	4.22	4.16		
	19.11	0.235	16.97	4.28	4.23		
	14.80	0.184	13.51	4.29	4.26		
	10.09	0.131	9.49	4.28	4.26		
	5.78	0.092	5.58	4.11	4.09		
283.15	30.38	0.351	25.26	4.28	4.20	90.76	92.68
	24.89	0.292	21.45	4.30	4.24		
	20.09	0.229	17.84	4.36	4.31		
	14.99	0.167	13.73	4.41	4.37		
	10.19	0.116	9.61	4.42	4.39		
	5.68	0.085	5.50	4.17	4.16		
288.15	31.75	0.311	26.44	4.44	4.37	96.54	98.00
	26.56	0.259	22.83	4.48	4.42		
	21.85	0.221	19.32	4.47	4.42		
	16.46	0.176	15.02	4.45	4.41		
	10.39	0.117	9.80	4.43	4.40		

	34.50	0.287	28.82	4.61	4.53		
	29.98	0.258	25.68	4.60	4.54		
298.15	25.48	0.219	22.37	4.63	4.57	108.34	110.15
	19.89	0.168	17.98	4.67	4.63		
	14.50	0.133	13.48	4.62	4.59		
	8.03	0.072	7.72	4.68	4.66		

For system CO₂ + n-hexane at 25⁰C, in the case when we have obtained the Henry's constants by using of Krichevsky-Kazarnovsky equation, we represented $\ln \frac{f_2^g}{x_2^l}$ versus pressure (figure 1), and when we used Krichevsky-Ilinskaya equation, we represented $\ln \frac{f_2^g}{x_2^l} - \frac{\bar{V}_2^\infty}{RT} \cdot (P - P_1^s)$ versus $[1 - (x_1^l)^2]$ (figure 2). In both cases we obtained a straight line that allow a good extrapolation of Henry's constants.

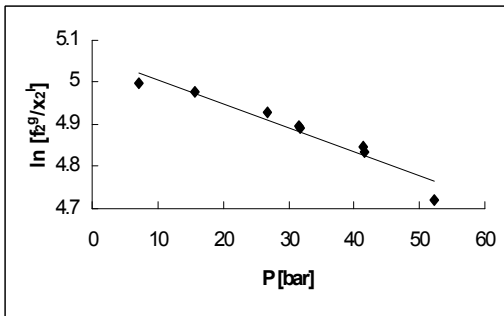


Fig. 1. Solubility of CO₂ in n-hexane at high pressures at 25⁰C (Krichevsky-Kazarnovsky equation)

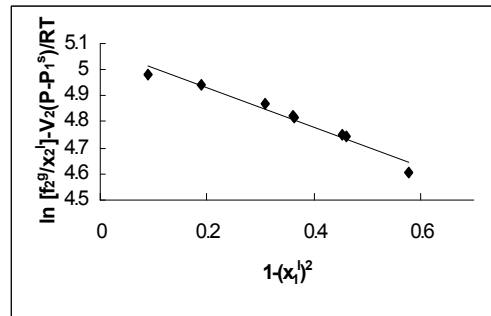


Fig. 2. Solubility of CO₂ in n-hexane versus molar fractions at 25⁰C (Krichevsky-Ilinskaya equation)

In figures 3 and 4 we represented the Henry's constants, $H_{2,1}^{P^s}$ (obtained from Krichevsky-Kazarnovsky and Krichevsky-Ilinskaya equations) versus temperature for both systems.

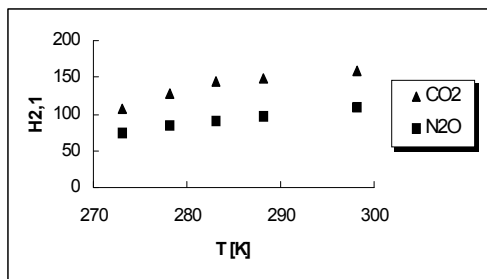


Fig. 3. Temperature dependence of Henry's constants for CO₂ and N₂O in n-hexane calculated with Krichevsky-Kazarnovsky equation

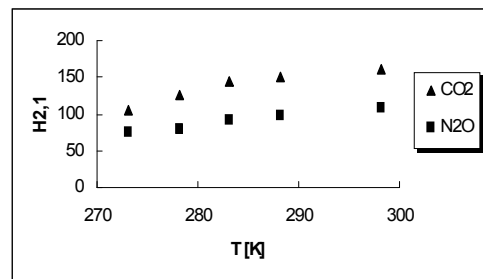


Fig. 4. Temperature dependence of Henry's constants for CO₂ and N₂O in n-hexane calculated with Krichevsky-Ilinskaya equation

We remark an excellent agreement between the values of Henry's constants calculated with the equation (7) and (11).

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