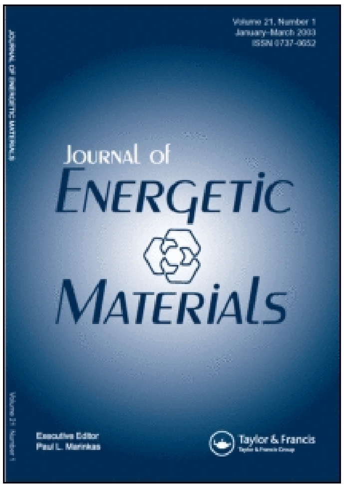

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The solubility of gases under pressure in liquid propellants

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THE SOLUBILITY OF GASES UNDER PRESSURE IN LIQUID PROPELLANTS

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ABSTRACT

A corresponding states correlation has been developed for the solubility of pure gases and mixtures in LGP 1846, a HAN based liquid propellant [1]. For nitrogen, methane, xenon, krypton, and argon, and their mixtures the correlation can be used to estimate gas solubilities for pressures upto 100 MPa in the temperature range 258 < T < 303 K. The correlation is in satisfactory agreement with all available experimental data for these systems. Dissolved gases are expected to significantly effect many physical and chemical properties of liquid propellant systems.

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INTRODUCTION

Aqueous solutions of hydroxyl ammonium nitrate (HAN), and aliphatic amine nitrates (AAN), posses excellent potential for use as high performance liquid propellants. One such propellant being actively considered is LGP 1846, which consists of 60.79, 19.19, and 20.02 weight percent of HAN, triethanol ammonium nitrate (TEAN), and water, respectively.[2]. The physical properties of these propellants are needed to model their behavior in the gun, where they can be under high pressures, and in contact with combustion gases. Since such gases can in general be expected to be soluble to some extent in the propellants, there is a need for a reliable method for predicting such solubilities, especially under high pressures. Dissolved gases are known to significantly affect many physical and chemical properties of aqueous solutions.

The corresponding states theory is a powerful tool for predicting thermodynamic and transport properties of fluids. However, the conditions that must be satisfied for the simple corresponding states principle to be valid are only obeyed by simple molecules like pure argon , krypton, and xenon [3]. In this paper we extend the simple corresponding states theory to include more complex substances that do not satisfy these conditions. This has been accomplished by replacing the critical parameters (usually temperature and volume) generally used in corresponding states, by two adjustable parameters. These parameters can be obtained from very limited experimental data. The technique used is similar in spirit to the shape factor method which has been widely used to predict thermodynamic and transport properties for a wide range of substances [4,5].

THEORY

The solubility of a gas in a liquid can be conveniently estimated via its fugacity. At equilibrium the fugacity of any component i must be equal in both the gas and liquid phases [6],

$$f_i^{(G)} = f_i^{(L)} \tag{1}$$

The fugacity in the gas phase can usually be estimated using generalized corresponding states charts,which are widely available [7], although if necessary it can be directly obtained from the relationship

$$RT\ln\left(\frac{f_i^{(G)}}{y_i P}\right) = \int_0^P \left(\bar{v}_i - \frac{RT}{P}\right)\frac{dP}{P} \tag{2}$$

where R is the universal gas constant, T the temperature, P the pressure, y_i the mole fraction of i in the gas phase, and $\bar{v}_i$ the partial molar volume of i. The integral in eqn. (2) can be evaluated using a suitable equation of state. For the more common substances, such equations of state are available [8].

For the liquid phase the fugacity can be estimated from [9],

$$f_i^{(L)} = \gamma_i^{*} x_i H_{i,S}^{0} \exp\left(\int_0^P \frac{\bar{v}_i dP}{RT}\right) \tag{3}$$

where $H_{i,S}^{0}$ is the Henry's constant in the solvent, γ_i the activity coefficient, and x_i the mole fraction of i in the solution. When $x_i \rightarrow 0$ (in practice less than 0.1), $\gamma_i^{*} \rightarrow 1$. Since we expect our solubilities to be rather low, and assuming $\bar{v}_i$ to be independent of pressure (an assumption generally acceptable up to 100 MPa), eqn. (3) can be simplified to

$$f_i^{(L)} = x_i H_{i,S}^0 \exp\left(\frac{P\bar{v}_i^\infty}{RT}\right) \qquad (4)$$

From eqns. (1) & (4), the solubility of the gas can be estimated as

$$x_i = f_i^{(G)} / H_{i,S}^0 \exp\left(\frac{P\bar{v}_i^\infty}{RT}\right) \qquad (5)$$

Thus in addition to $f_i^{(G)}$, to predict the solubility of gases in liquid propellants, data is needed on $H_{i,S}^0$ and $\bar{v}_i^\infty$ In the next section we describe how these can be estimated using corresponding states.

RESULTS

The fugacity of component i in the gas phase can be obtained using generalized corresponding states tables or charts, e.g., those provided in Lewis and Randall [7]. For pure gases,

$$(f/P)_i^{Pure} = (f/P)^0[(f/P)^1]^\omega \qquad (6)$$

where $(f/P)^0$ and $(f/P)^1$ are generally given as a function of reduced temperature and pressure, and ω is the Pitzer acentricity factor [9]. For mixtures , one can generally make the assumption of ideal mixing , especially when the constituents of the mixture have similar chemical structure. In such cases the fugacity of component i in a mixture is given by

$$f_i^{(G)} = y_i f_i^{Pure} \tag{7}$$

To test the accuracy of this generalized corresponding states method for fugacity for the gases of interest to us, we also calculated fugacities using the rigorous definition of eqn. (2), using accurate equations of state. Both the methods showed excellent agreement. For mixtures we used a revised Redlich - Kwong equation [10] with eqn. (2).

Henry's constants for gases in solvents can be estimated from solubility data at atmospheric pressure and eqn. (5).

$$H^0_{i,S} = P/x_i \, , \tag{8}$$

since at low pressures $f_i^{(G)} \to P$ and $P\bar{V}_i^{\infty}/RT \to 0$. Experimental data on the solubility of various simple gases in LGP 1846 has been measured recently by Koski [11]. We have used this data to obtain a generalized correlation for Henry's constant,

$$H^{\bullet}_{i,S} = -206.7 + 3.992\,T^{\bullet} - 0.0126\,T^{\bullet 2} \, , \tag{9}$$

where $H^{\bullet}_{i,S} = H^0_{i,S}/\beta_i$ and $T^{\bullet} = T/\alpha_i$. Values of α_i and β_i for various gases in LGP 1846 are given in Table 1. Figure 1 shows a comparison of values for Henry's constants from the corresponding states correlation given by eqn (9), and the available experimental data. As can be seen, the correlation represents the data quite accurately.

There are no experimental measurements available for $\bar{V}_i^{\infty}$ of the gases studied here in LGP 1846. However experimental data is available for $\overline{V}_i^{\infty}$ in water and other concentrated aqueous electrolyte solutions. Eqn. (2) applied to the solubility of gases in water and electrolyte solutions leads to the expression

$$\frac{x_i^{W}}{x_i^{ES}} = \frac{H_{i,ES}^{0}}{H_{i,W}^{0}} \exp\left[\frac{P(\overline{V}_{i,ES}^{\infty} - \overline{V}_{i,W}^{\infty})}{RT}\right] \qquad (10)$$

An examination of experimental data [12,13] on gas solubilities in water, and aqueous electrolyte solutions at pressures between 0.1 and 60 MPa, clearly shows that although x_i^{W}/x_i^{ES} is a function of temperature, it is independent of pressure. From the form of eqn (10), this can only be possible if $\overline{V}_{i,ES}^{\infty} = \overline{V}_{i,W}^{\infty}$. We have extended this result to LGP 1846 and approximated $\overline{V}_i^{\infty}$ data in water as $\overline{V}_i^{\infty}$ for these gases in LGP 1846. Such "experimental data" for $\overline{V}_i^{\infty}$ was then fitted to a generalized corresponding states correlation,

$$V_i^{*} = -0.0156 + 33.26T^{*}, \qquad (11)$$

where $V_i^{*} = \overline{V}_i^{\infty} P_i^{c}/RT_i^{c}$ and $T^{*} = TP_i^{c}/C_S T_i^{c}$.

Here P_i^{c} and T_i^{c} are the critical pressure and temperature of i, and C_S is the cohesive energy density of LGP 1846, originally introduced by Scatchard and Hildebrand in developing the regular solution theory [6]. Since water is the only volatile substance in LGP 1846 at temperatures of interest to us, this would essentially be the value for water. Figure 2 shows a comparison of $\overline{V}_i^{\infty}$ values predicted using the corresponding states correlation of eqn. (11), and available experimental data [12,13]. In view of the relatively large uncertainties in such experimental measurements, the correlation is quite satisfactory.

The solubility of gases under pressure can now be obtained by using eqn (5). The fugacity in the gas phase can be obtained using the correlations available in the literature (see eqns 6 and 7). The Henry's constants required in eqn (5), can be obtained from the correlation developed here (eqn 9), and the partial molar volumes from eqn (11). Experimental data is not available for the solubility of gases in liquid propellants, at high pressures. It is therefore not possible to test our method for liquid propellants. However, limited data is available on gases in aqueous solutions such as sodium chloride. In Figure 2A we have compared results obtained using the technique outlined above with experimental data for N_2 in aqueous sodium chloride [12]. The results confirm the general validity of assumptions we have made for a wide range of pressures.

The results for five pure gases (Ar, Kr, Xe, N_2 and CH_4).are shown in Figures 3 to 7. The solubility increases with pressure, but the rate of increase of solubility with pressure decreases with increasing pressure. The solubility also increases with temperature at low and moderate pressures, but it appears that there may be an inversion in this temperature dependence at high pressures (around 100 MPa). Although, this inversion is within the estimated accuracy of our predictions, it is clear, that the temperature dependence of solubility varies considerably over the pressure range 0 to 100 MPa. The behavior of xenon is somewhat different from that of the other simple gases. This is because the critical temperature of xenon is 289.7 K, which is close to the ambient temperatures studied here.

The solubility of simple gas mixtures in LGP 1846 is shown in Figures 8 and 9 for N_2-CH_4 and Ar-CH_4 , respectively, for three compositions. The solubility of the mixture as a function of pressure increases as the mole fraction of the component with the higher critical pressure increases. The solubility of the Ar-CH_4 mixture does not vary much with composition, as the critical pressures of the two are very close to each other, although there seems to be an inversion in the composition dependence at around 700 atm. This again is within the estimated accuracy of our predictions. The pressure dependence of the solubility is similar and the temperature dependence is expected to be the same as for the pure gases. Similar results are obtained for Ar-$N_2$and Kr-CH_4 mixtures.

CONCLUSIONS

We have developed a technique for predicting solubilities of gases in LGP 1846. This technique could be extended to other aqueous electrolyte solutions, and work is currently in progress to enable such an extension. All the correlations used are based on the corresponding states principle, which has been found to be a very powerful method for such predictions by us and others [4,5]

ACKNOWLEDGEMENTS

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Table 1

GAS	α_i	$10^{-3}\beta_i$
Nitrogen	1.52	3.220
Methane	1.64	1.220
Xenon	2.64	0.373
Krypton	1.99	0.566
Argon	1.74	1.350

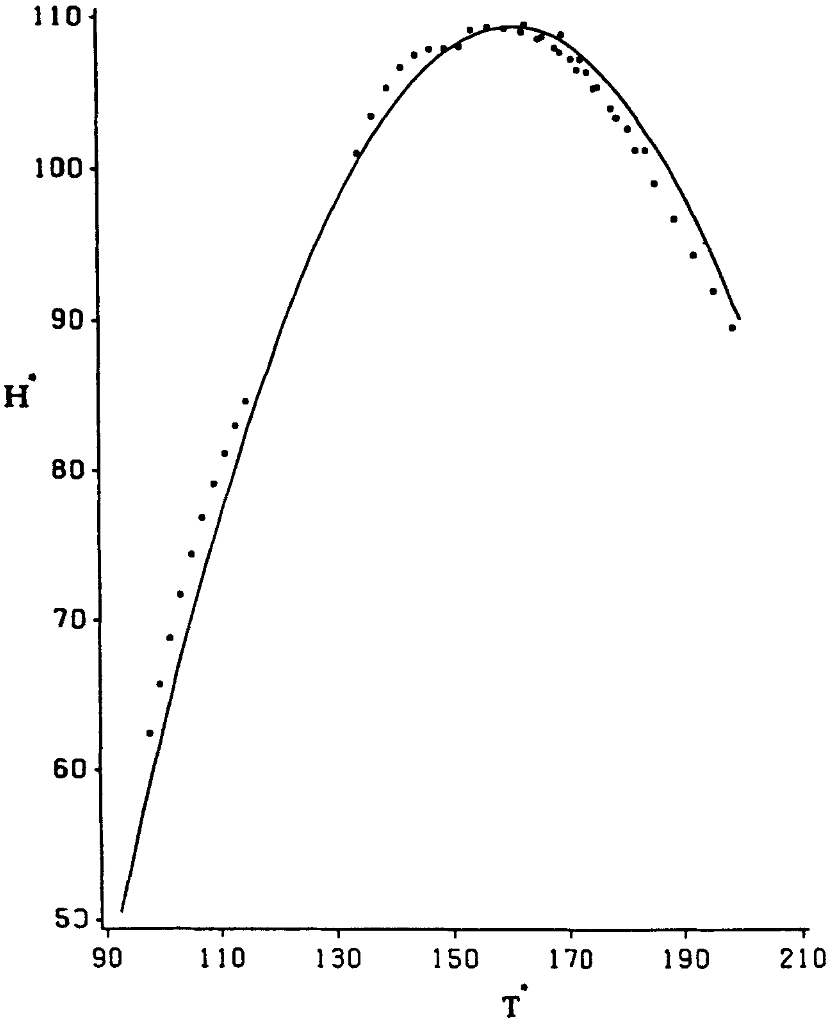

Fig. 1: The calculated (eqn. 9) and experimental values of Henry's constants; ___ calculated, • experimental.

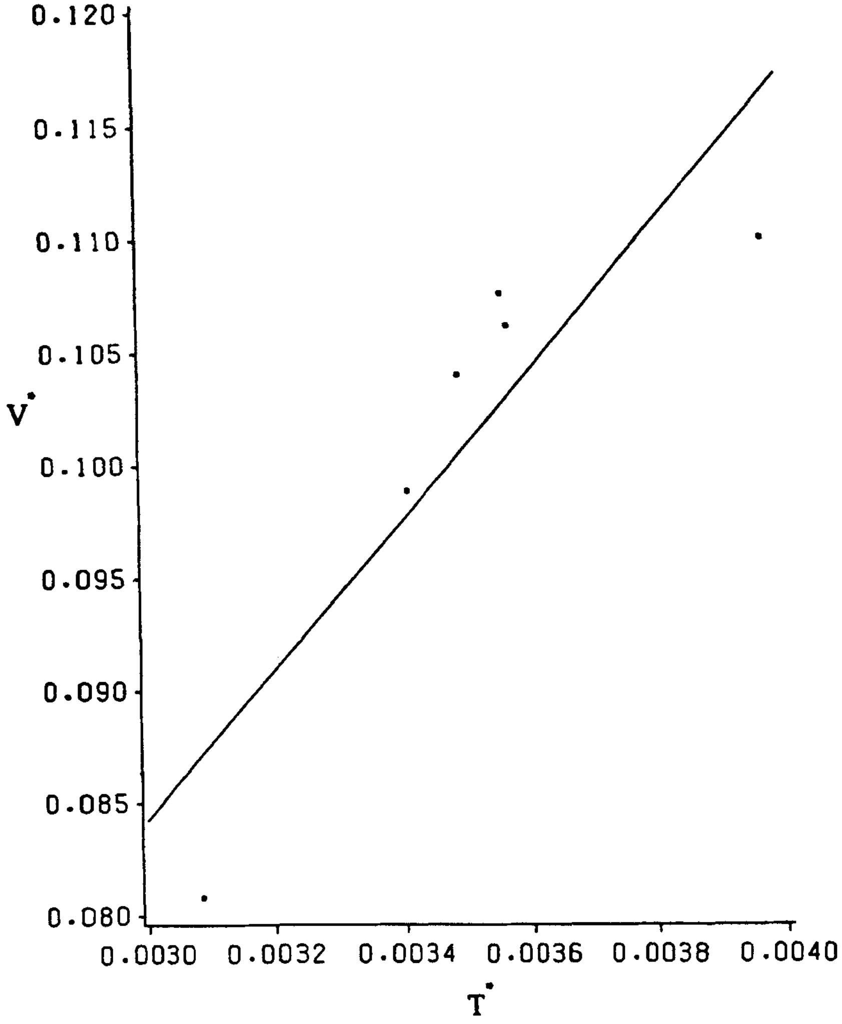

Fig. 2: The calculated (eqn. 11) and experimental values of partial molar volumes; ___ calculated, ● experimental.

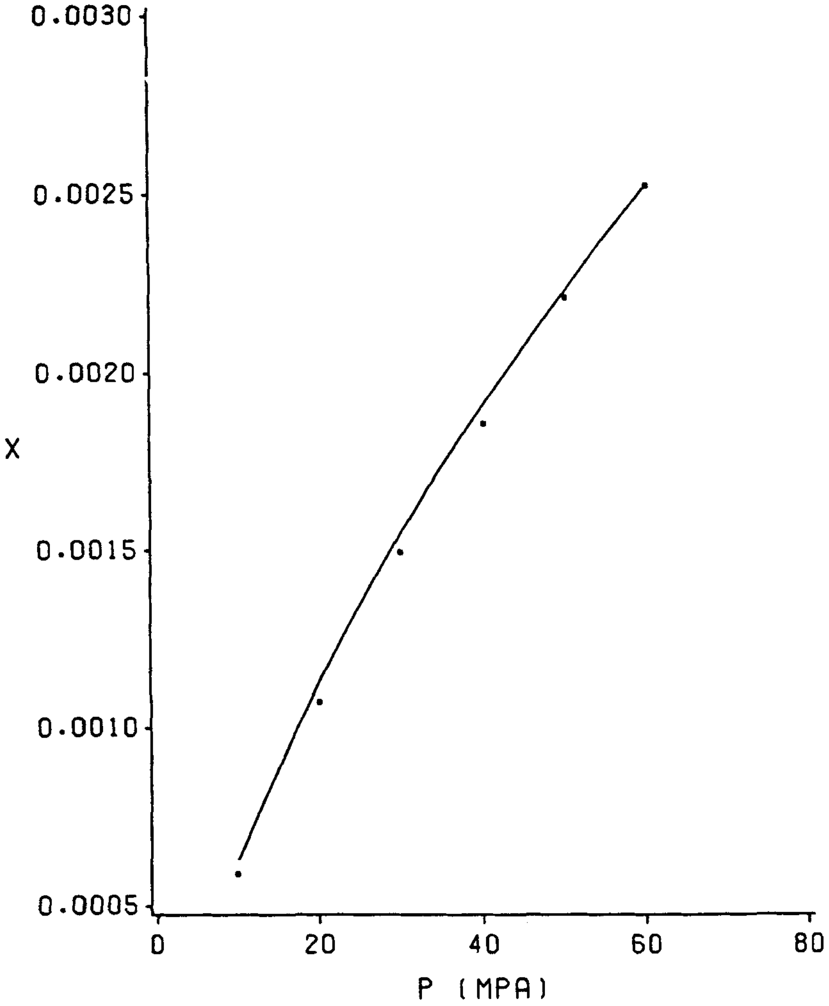

Fig. 2A: The calculated and experimental solubilities of nitrogen in 1 m aqueous sodium chloride. ___ calculated, ● experimental [12].

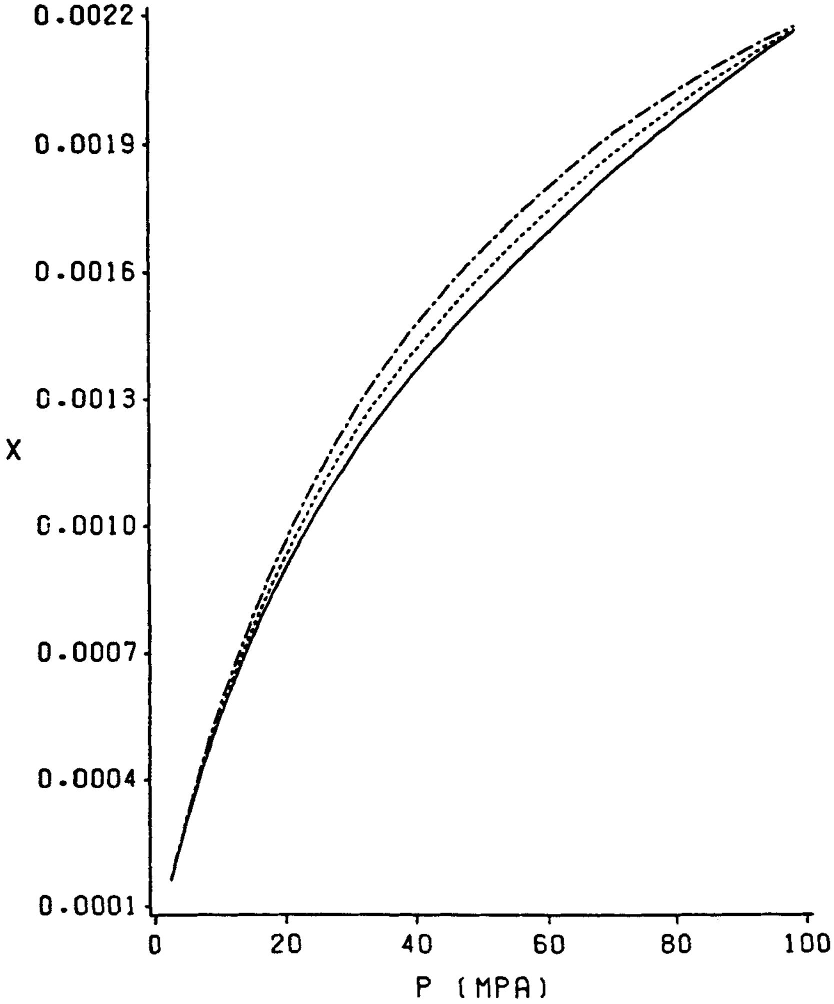

Fig. 3: The estimated solubility of argon in LGP 1846; _._ 30, --- 15, ___ 0 Deg. C.

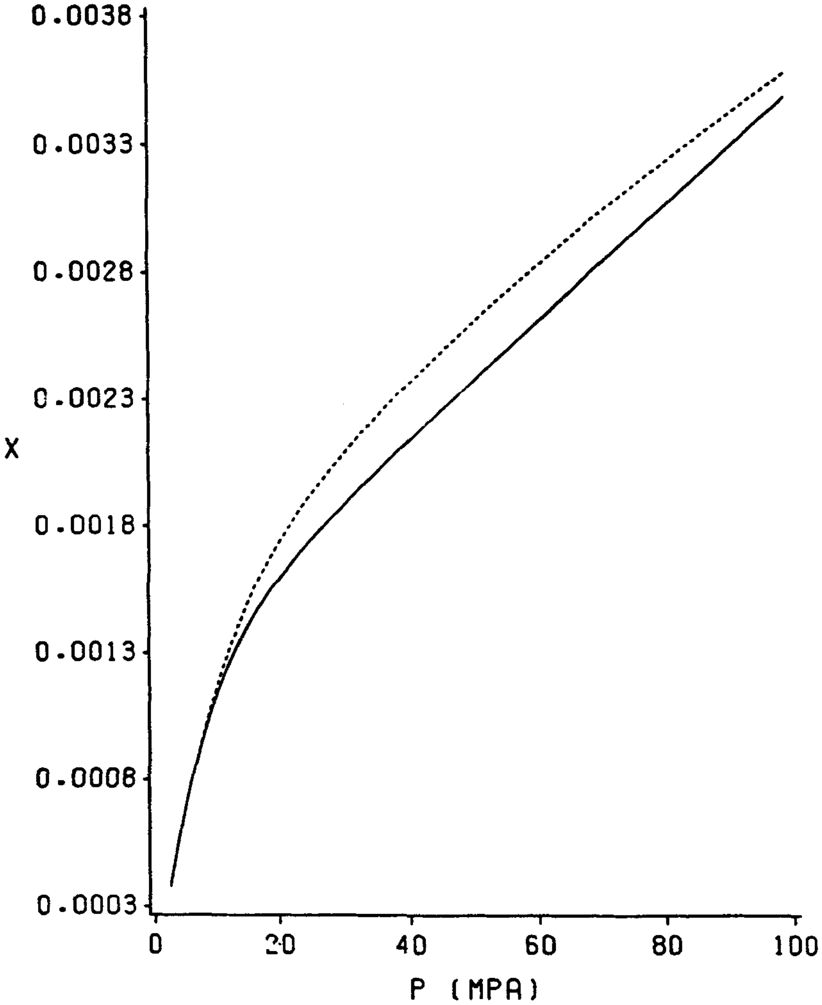

Fig. 4: The estimated solubility of krypton in LGP 1846; ---25, ___ 0 Deg. C.

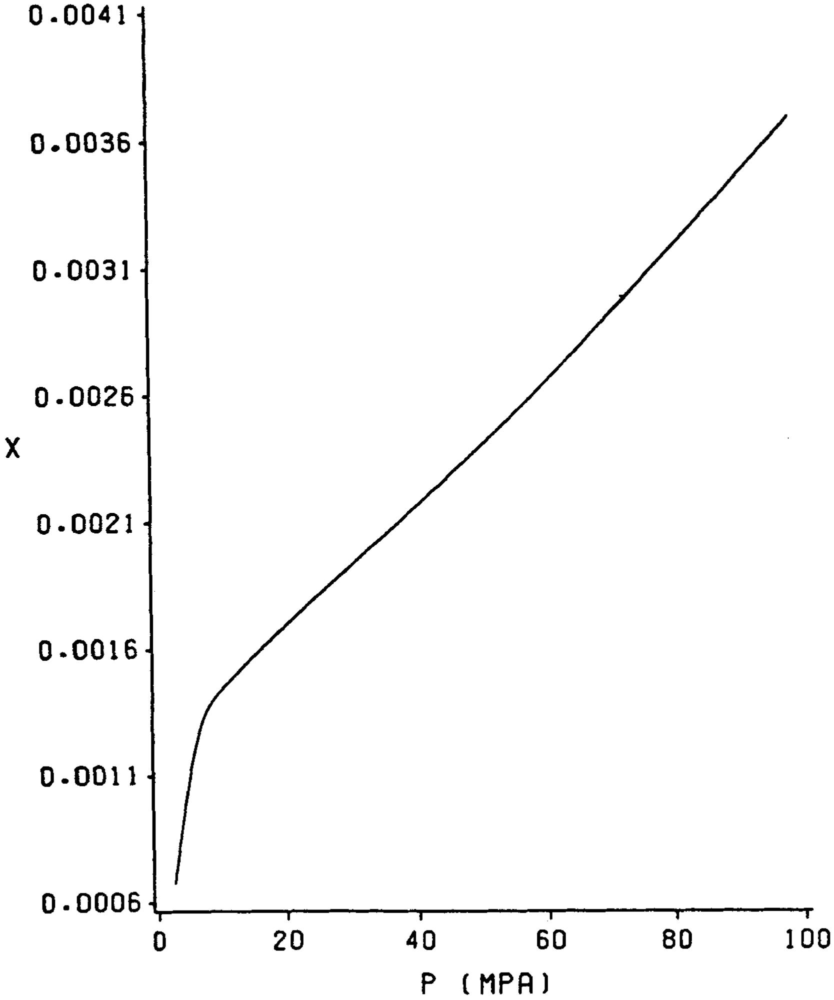

Fig. 5: The estimated solubility of xenon in LGP 1846 at 30 Deg. C.

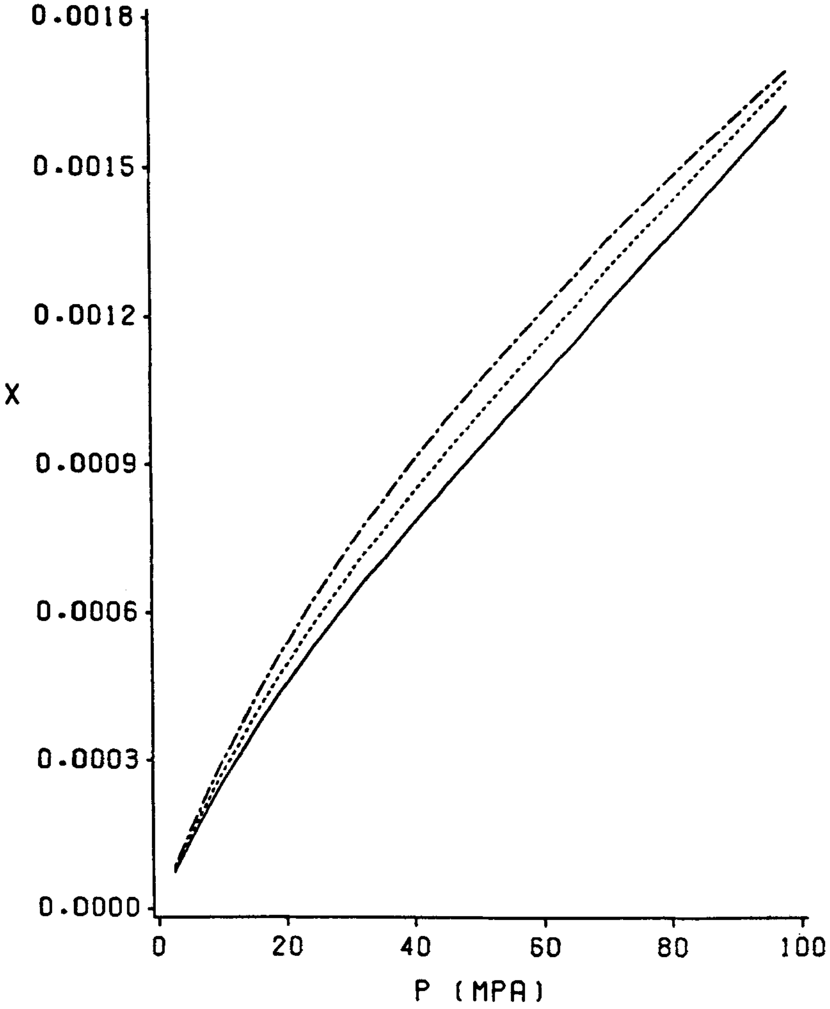

Fig. 6: The estimated solubility of nitrogen in LGP 1846; _._ 30, --- 15, ___ 0 Deg. C.

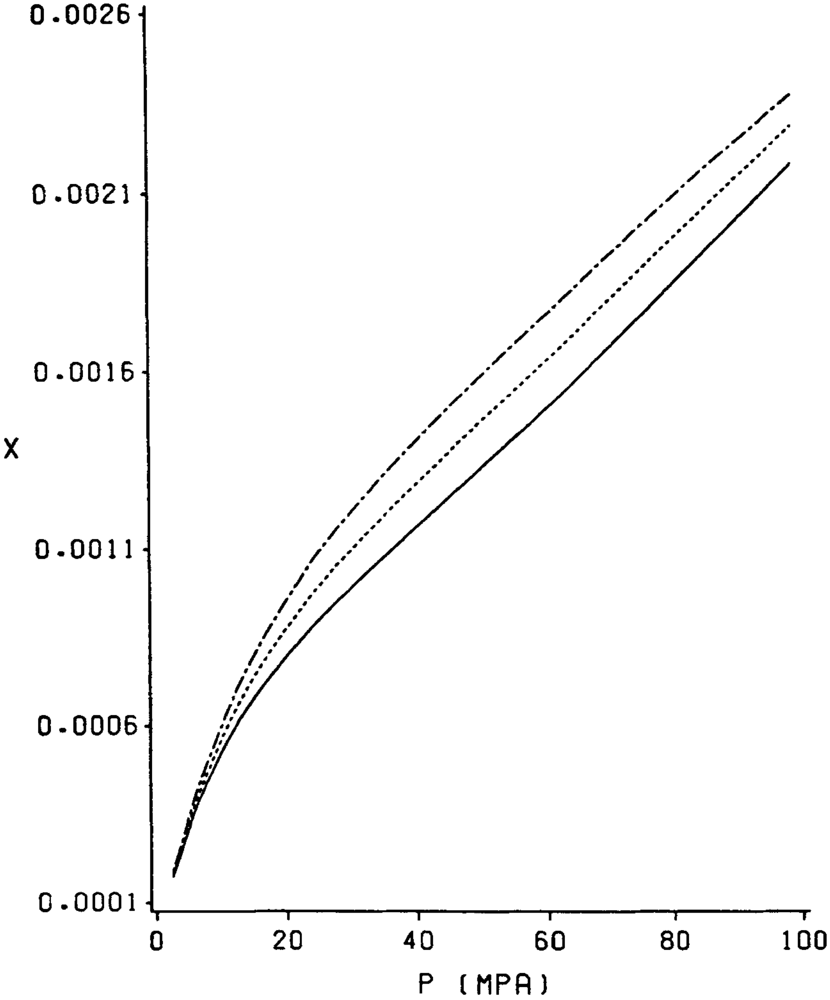

Fig. 7: The estimated solubility of methane in LGP 1846; _._ 30, --- 15, ___ 0 Deg. C.

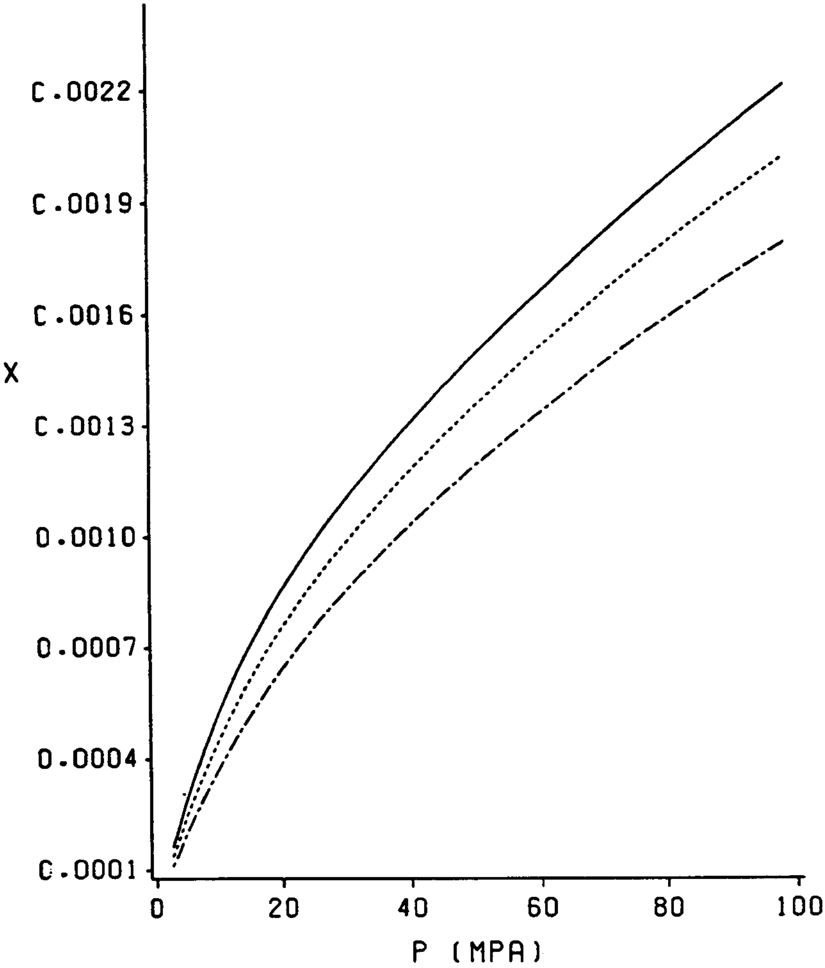

Fig. 8: The estimated solubility of nitrogen-methane mixture in LGP 1846 at 30 Deg. C; ___ 75, --- 50, _._ 25 mole% methane.

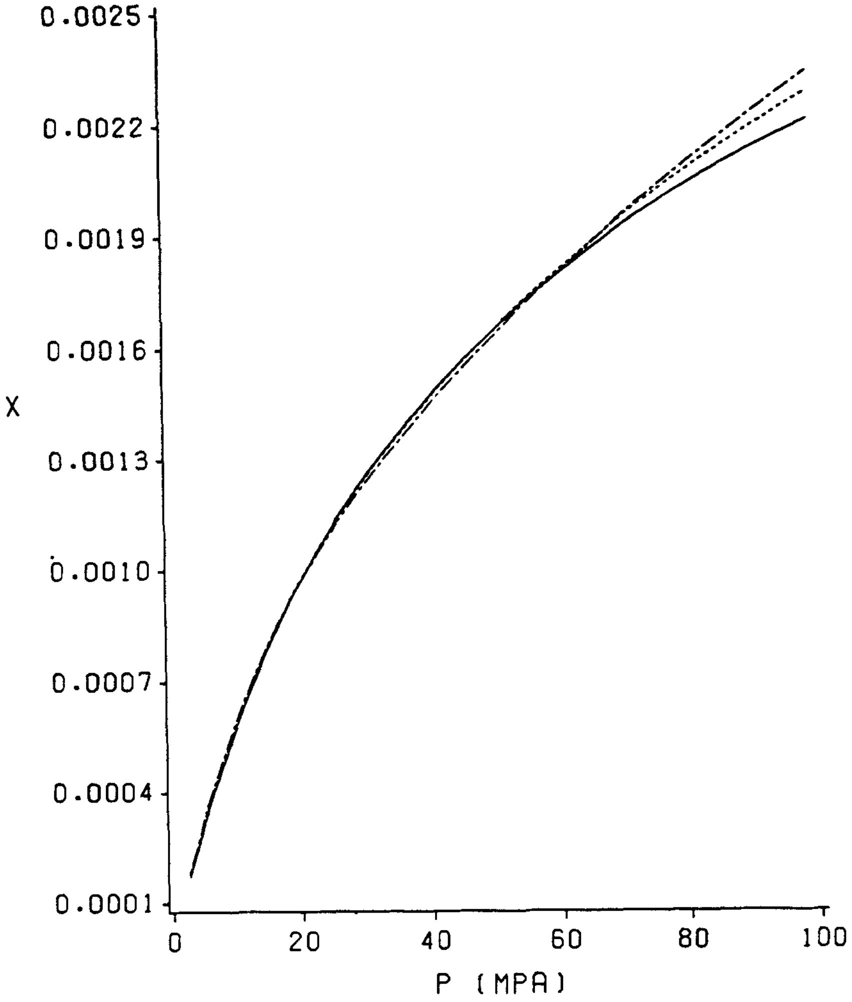

Fig. 9: The estimated solubility of argon-methane mixture in LGP 1846 at 30 Deg. C. _._ 75, --- 50, ___ 25 mole% methane.