

the calculated Boyle temperature were unchanged) would be consistent with the type of change made by Alder and Paulson¹⁰ for stabilizing the crystal lattices. This may also account for the relative success of the $\exp(-6)$ potential for predicting crystal properties since its slope is greatest in the region $1.35 < r/V_B^{1/3} < 1.45$. Whether other quantitative agreement may be obtained must await calculations using potential models which were changed in this manner.

Conclusion

We have considered a number of properties of the noble gases predicted by realistic analytical potential

functions, particularly the Kihara core model. Second virial coefficients, viscosities, and diffusivities may all be predicted satisfactorily except at very low and at very high temperatures, but results for the isotopic thermal diffusion factor, coefficients on the dispersion terms, and crystal properties indicate that the attractive region of our present models may need modification.

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Thermodynamic Properties of Gases in Propellants. II. Solubilities of Helium, Nitrogen, and Argon Gas in Hydrazine, Methylhydrazine, and Unsymmetrical Dimethylhydrazine

by E. T. Chang, N. A. Gokcen, and T. M. Poston

*Chemical Thermodynamics Section, Laboratories Division, Aerospace Corporation, El Segundo, California 90045
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Solubilities of He, N₂, and Ar in liquid hydrazine, methylhydrazine, and unsymmetrical dimethylhydrazine have been measured at various pressures and temperatures. The results show that Henry's law is obeyed and the standard change of Gibbs energy, ΔG° , is linear in temperature. The standard heat of solution, ΔH° , and the entropy of solution, ΔS° , have been obtained, and ΔG° has been expressed as a linear function of temperature. The change in the solubility of a chosen gas from one solvent to another has been correlated by using the Lennard-Jones 6-12 potential with the assumption that the solute interacts with a hard core studded with H atoms. The functional forms of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ for He, N₂, and Ar in symmetrical dimethylhydrazine have been obtained from such correlations and the method is shown to be useful for similar gas-liquid systems. It is shown that: (a) the changes in the solubilities follow the changes in the dipole moments of liquids, and (b) the entropy of solution varies linearly with the logarithm of mole fractions of solutes in methylhydrazine and in unsymmetrical dimethylhydrazine, but not in hydrazine.

Introduction

Practical difficulties in pressurizing, storing, and pumping liquid propellants require accurate data on the solubilities of gases in these liquids. A series of investigations was therefore initiated to measure the solubilities of the most important propellant pressurization gases. The first part of this investigation,¹ hereafter referred to as part I, dealt with the solubil-

ities of He, N₂, O₂, Ar, and N₂O₃ in liquid N₂O₄, and, the second part, which is the present paper, deals with the solubilities of He, N₂, and Ar in liquid hydrazine, methylhydrazine (MH), and unsymmetrical dimethylhydrazine (UDMH).

There are no available data² on the solubilities in the

(1) E. T. Chang and N. A. Gokcen, *J. Phys. Chem.*, **70**, 2394 (1966).

foregoing binary systems, each consisting of a gas and a liquid. In addition, supplementary data, such as the values of density and vapor pressure for each liquid at various temperatures,² were found to be inadequate for the desired accuracy in the measurements of solubilities. It was therefore necessary to obtain such data concurrently with the solubility measurements.

Experimental Section

The apparatus for solubility measurements was described in part I. Briefly, it consisted of three calibrated volumes for the measurements of admitted gases, a container for the propellant, which was stirred with a glass-enclosed magnet bar, and a manometer for measuring the pressure with a microslide cathetometer. The volume occupied by the liquid was determined from the weight and the density measurements. Since the available data on the densities were not accurate enough for this investigation, the following equations were obtained from the precise data obtained by a method described elsewhere in detail.³

$$\rho(\text{N}_2\text{H}_4) = 1.02492 - 0.000865t \quad (1)$$

$$\rho(\text{MH}) = 0.89338 - 0.000943t \quad (2)$$

$$\rho(\text{UDMH}) = 0.80980 - 0.001030t \quad (3)$$

In the foregoing equations, ρ is the density in g/ml, and t is the temperature in °C. The gas and the liquid were brought to equilibrium at a constant temperature by violently stirring the liquid. The amount of dissolved gas was found by subtracting the amount of remaining gas from that of admitted gas. The procedure was checked for the solubility of nitrogen in water and the result agreed within 2% of published data.

The method differed from that in part I because of the change in the vapor pressure of MH and UDMH with time. These propellants, in initially distilled, pure state, dissociate slightly to yield increasing observed vapor pressure, irrespective of the history of their treatment and subsequent methods of handling and the degree of exposure to light. The change in vapor pressure decreases exponentially with time, hence the pressure was monitored for 2 hr and the further change during the solubility measurements was obtained by extrapolation. An uncertainty of 0.3 mm in the vapor pressure caused a small unavoidable error in the solubility. The vapor pressure of hydrazine was found to be very nearly independent of time.

Results

The results on the solubilities of He, N₂, and Ar in hydrazine, MH, and UDMH are listed in Table I. Since the mole fraction of each dissolved gas is small, Henry's law is obeyed, *i.e.*, the solubility is proportional to the partial pressure of gas. This is substantiated by the measurements at various pressures,

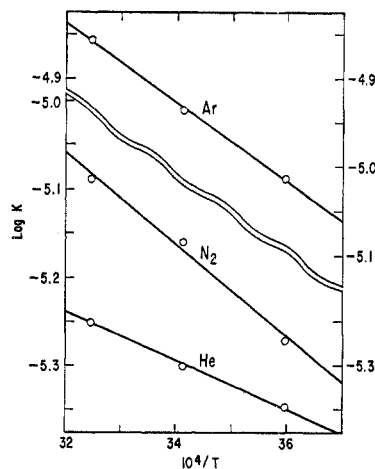
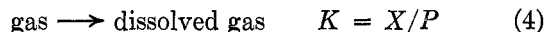


Figure 1. Solubilities of He, N₂, and Ar in liquid N₂H₄.

and, further, it shows that there are no chemical reactions between nitrogen and the solvents.¹ The process of dissolution may be represented by



where X is the mole fraction, P is the partial pressure of dissolved gas, and K may be considered as the equilibrium constant or the inverse of Henry's law constant. The values of K , which are also the atmospheric solubilities, are listed in Table I. They are about 15 times lower for He in hydrazine than the corresponding values¹ for He in N₂O₄.

The average values of K for the gases in hydrazine are represented in Figure 1 as $\log K$ vs. $10^4/T$, where T is in °K. The equations for the straight lines, obtained by the least-squares method, are related to the standard Gibbs energy change, ΔG° , of reaction 4 by $\Delta G^\circ = -RT \ln K$, and they are represented by

$$\Delta G^\circ(\text{He in N}_2\text{H}_4) = 1260 + 19.94T \quad (5)$$

$$\Delta G^\circ(\text{N}_2 \text{ in N}_2\text{H}_4) = 2360 + 15.60T \quad (6)$$

$$\Delta G^\circ(\text{Ar in N}_2\text{H}_4) = 2040 + 15.61T \quad (7)$$

The standard state for gases is 1 atm and the reference state for dissolved gases is infinitely dilute solution in eq 5-7. Deviations from ideality for gases are much smaller than the experimental errors, hence they have been ignored.

The average values of K at each temperature for the gases in MH are represented in Figure 2 and expressed by eq 8-10.

(2) In addition to the usual reference sources the following summaries also do not contain any such data: (a) R. R. Liberto, "Titan II Storable Propellant Handbook," Report No. 8111-933003 AFFTC TR-61-32, Bell Aerosystems Co., Buffalo, N. Y., June 1961; (b) "Pressurization Systems Design Guide," Vol. IIB, Aerojet General Corp., Azusa, Calif., Dec 1965; (c) "Liquid Propellant Manual," CPIA, Johns Hopkins University, Silver Spring, Md., 1961.

(3) A. I. Kemppinen and N. A. Gokcen, *J. Phys. Chem.*, **60**, 126 (1956).

Table I: Solubilities of He, N₂, and Ar in N₂H₄, MH, and UDMH^a

	<i>T</i>	He			N ₂			Ar		
		<i>P</i>	10 ³ <i>X</i>	10 ³ <i>K</i>	<i>P</i>	10 ³ <i>X</i>	10 ³ <i>K</i>	<i>P</i>	10 ³ <i>X</i>	10 ³ <i>K</i>
N ₂ H ₄	278.15	1.2333	0.51	0.41	1.1453	0.56	0.49	1.1417	1.04	0.91
		2.1927	1.08	0.49	2.0836	1.21	0.58	2.1233	2.20	1.03
			Av 0.45			Av 0.54			Av 0.97	
	293.16	1.1411	0.52	0.46	1.0492	0.69	0.66	0.9160	1.03	1.13
		2.0451	1.10	0.54	1.1120	0.71	0.64	1.7985	2.13	1.19
			Av 0.50		1.9719	1.45	0.74		Av 1.16	
	308.18				2.0619	1.51	0.73			
					Av 0.69					
		1.0902	0.57	0.52	1.0842	0.84	0.78	1.0567	1.44	1.36
		1.3121	0.68	0.52	2.1112	1.80	0.85	2.0129	2.85	1.42
		1.9941	1.17	0.59						
		2.3070	1.44	0.62		Av 0.82			Av 1.39	
			Av 0.56							
MH	253.24	0.8264	1.15	1.39	0.9786	6.48	6.62	1.1165	16.65	14.91
		1.9837	3.12	1.57	2.0042	13.39	6.68	2.0127	29.75	14.77
			Av 1.48			Av 6.65			Av 14.8	
	273.15	1.1448	2.04	1.78	1.1052	8.34	7.55	1.1685	18.59	15.91
		2.1454	4.18	1.95	1.9863	15.02	7.56	2.0344	32.60	16.02
			Av 1.86			Av 7.56			Av 16.0	
	298.14	1.1272	2.78	2.46	1.0577	9.78	9.25	1.1680	21.00	17.98
		2.0617	5.41	2.63	2.0856	19.46	9.33	2.0182	36.40	18.04
			Av 2.54			Av 9.29			Av 18.0	
	253.05	1.1719	5.83	4.97	1.2330	36.64	29.71	0.9695	62.43	64.39
		2.0347	10.03	4.93	1.9703	58.44	29.66	1.9448	125.2	64.36
			Av 4.95			Av 29.7			Av 64.4	
		1.3684	9.19	6.72	1.0005	32.59	32.57	1.1590	76.35	65.87
		2.2511	15.51	6.89	1.3281	43.48	32.74	1.9894	131.0	65.87
			Av 6.80		2.0717	68.08	32.86		Av 65.9	
UDMH	273.15					Av 32.7				
		1.4394	12.53	8.70	1.1587	42.70	36.85	0.9585	65.84	68.69
		2.2158	19.81	8.94	1.9251	71.30	37.04	1.7669	121.5	68.75
	293.16		Av 8.82			Av 36.9			Av 68.7	

^a *T*, °K; *P*, atm; *X*, mole fraction; *K* = *X*/*P*.

$$\Delta G^\circ(\text{He in MH}) = 1800 + 15.01T \quad (8)$$

$$\Delta G^\circ(\text{N}_2 \text{ in MH}) = 1120 + 14.71T \quad (9)$$

$$\Delta G^\circ(\text{Ar in MH}) = 650 + 14.97T \quad (10)$$

Similar data for the gases in UDMH, shown in Figure 3, yield

$$\Delta G^\circ(\text{He in UDMH}) = 2110 + 11.36T \quad (11)$$

$$\Delta G^\circ(\text{N}_2 \text{ in UDMH}) = 800 + 13.00T \quad (12)$$

$$\Delta G^\circ(\text{Ar in UDMH}) = 240 + 13.67T \quad (13)$$

Discussion

The process of dissolution of N₂ in all the propellants is that shown by reaction 4, and not by any other reaction because of the following reasons: (1) *K* is independent of pressure, and (2) the values of ΔH° in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ in eq 5–13 are of comparable magnitude and follow a reasonable pattern of variation from one gas to another, hence N₂ behaves like He and Ar, which do not react chemically with the propellants.

It is difficult to treat the solubilities of gases in these propellants by means of any reasonable molecular or geometrically abstract models⁴ because, first of all,

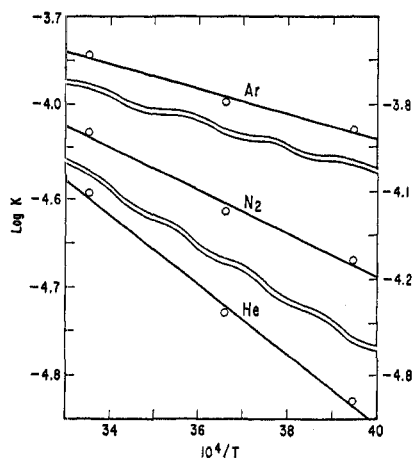


Figure 2. Solubilities of He, N₂, and Ar in liquid methylhydrazine.

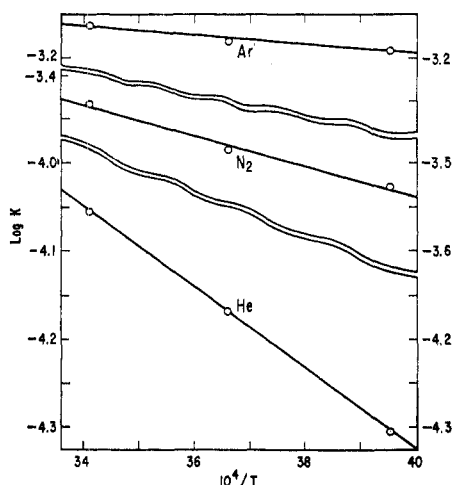


Figure 3. Solubilities of He, N₂, and Ar in unsymmetrical dimethylhydrazine.

the molecules of the methylhydrazines are complex, and, further, the molecular parameters necessary for such treatments are not known. Therefore, we shall be satisfied with a reasonable semitheoretical correlation of the data. For this purpose, we make the following assumptions. (1) The change in the standard Gibbs energy of solution of a particular gas from one liquid to another is caused by the change in the Lennard-Jones 6-12 potential⁵ in which the term involving $1/r^6$ is neglected, and that involving $1/r^{12}$ is taken into account so that

$$u \cong \frac{\alpha}{r^{12}} \quad (14)$$

In this equation u is the change in potential energy of a molecule as a function of distance r of approach to another molecule, and α is a constant related to the interaction energy and the minimum point in the potential energy curve. (2) The solubility of a gas varies from one solvent to another because ΔG°

varies, in accordance with eq 14, as the distance between the solute and solvent molecules, r , varies at a selected reduced temperature T_r , related to the melting point of propellant, T_m , by

$$T_r = T/T_m \quad (15)$$

(3) The distance r was computed in the following manner. First, the liquid is divided into cells, each containing one molecule of propellant, by dividing the molar volume by Avogadro's number. The solute could locate itself at the center of line connecting two molecules along a cubic diagonal. The value of r is the distance between the solute and solvent molecule minus the impenetrable distance of the solvent molecule, D . The value of D was obtained from the volume of the molecule by considering the outer hydrogen atoms as point masses. This volume was converted into a sphere whose radius was taken to be identical with D . In essence, the sphere having a radius of D was assumed to be studded with the hydrogen atoms, and the value of r in eq 14 is simply the distance between the centers of the solute and of the hydrogen atoms. As an example, we use the following data for UDMH: N-N = 1.45, N-H = 1.04, N-C-H = 2.56, which are the distances from the initial to final atom in ångströms, and the bond angle H-N-N is 110°, yielding an impenetrable molecular volume of 25.5 in cubic ångströms since the molecule forms the frustum of a cone. We convert this volume to a spherical volume whose radius gives the impenetrable distance D . The reason for this conversion of volume is that in the liquid state both the solute and the solvent molecules move randomly. The results at $T_r = 1.11$ are presented in Figure 4. The correlation is linear and it supports our assumptions.

It is now possible to estimate ΔG° for the solubilities of He, N₂, and Ar in symmetrical dimethylhydrazine (SDMH) from the linear correlation in Figure 4. For this purpose, it is also necessary to plot ΔG° vs. r^{-12} at $T_r = 1.30$. The point of intersection of r^{-12} for SDMH, which is the vertical dotted line in Figure 4, with each line gives ΔG° for that gas in SDMH. The values of ΔG° at $T_r = 1.11$ and $T_r = 1.30$ for each gas yields ΔG° as a linear function of temperature, T , in °K. The results are

$$\Delta G^\circ(\text{He in SDMH}) = 2490 + 7.70T \quad (16)$$

$$\Delta G^\circ(\text{N}_2 \text{ in SDMH}) = 1300 + 8.51T \quad (17)$$

$$\Delta G^\circ(\text{Ar in SDMH}) = 720 + 9.05T \quad (18)$$

Similar estimates can also be made for the remaining methyl compounds of hydrazine with a good deal of confidence. This procedure is also recommended for

(4) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworth Co. Ltd., London, 1959.

(5) J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A106**, 463 (1924).

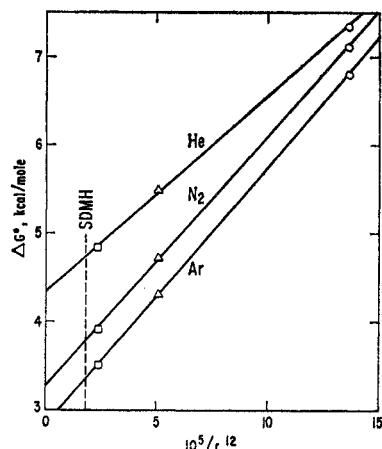


Figure 4. Variation of standard change in Gibbs energy of solution, ΔG° , with distance of approach, r , of solute and solvent molecules at $T = 1.11T_m$: O, in N_2H_4 ; Δ , in MH; and \square , in UDMH. T_m is the melting point in $^\circ K$, and r is in \AA stroms.

attaining reasonable estimates for the ethyl compounds of hydrazine.

We consider next the ideal, or Raoultian, solubility of He, N_2 , and Ar in a liquid exhibiting no interaction with the solute gas. The ideal solubility is computed by calculating the vapor pressure P_1^v of hypothetically existing liquids and setting the mole fraction X_1 equal to $1/P_1^v$ where 1 in the numerator is simply the atmospheric pressure. The results taken from Hildebrand and Scott⁶ are shown in Table II, together with other data on solubilities and dipole moments,⁷ μ . It is evident that the ideal solubility gives only a rough order of magnitude and it is likely to yield a closer value for the systems in which ΔH° of solution is negative and not too far from the heat of condensation of dissolved gases. Variation of the solubilities with the dipole moments, μ , follows the pattern⁸ shown in Table II, *i.e.*, the solubilities decrease with μ as μ increases from 0 to 1.9, and then they increase with μ larger than 1.9, although there are notable exceptions.

It has been shown by Hildebrand, *et al.*,⁸ that the

Table II: Comparison of Solubilities of He, N_2 , and Ar in Various Solvents² at 25° and 1 Atm ^{a, b}

Solvent	μ , D.	He	N_2	Ar
Ideal	...	16°	100	160
Cyclohexane	0.28 ^d	12.2	72.2	148
$N_2O_4^c$	0.6	10.2	65.8	98.4
Hydrazine ^c	1.9 ^d	0.52	0.72	1.24
Water	1.9	0.7	1.2	2.5
MH ^c	2.2 ^d	2.51	9.17	17.9
UDMH ^c	2.5 ^d	9.38	37.5	68.9
Acetone	2.8	10.8	59.2	90.6

^a All data, unless otherwise noted, are obtained from Hildebrand and Scott.⁶ ^b Numbers represent mole fraction $\times 10^5$. ^c Authors' values of solubility. ^d Dipole moments are from McClellan,⁷ the value for UDMH has been estimated by the authors from a plot of boiling point vs. μ^2 .

entropy of solution, $\bar{S}(\text{in soln}) - S(g)$, where \bar{S} is the partial molar entropy of dissolved gas in the solvent, for various gases plotted vs. the logarithm of mole fraction of solute at 1 atm yields a straight line for each solvent at a chosen temperature. This correlation is very good for MH and UDMH, fair for the gases¹ in liquid N_2O_4 , and very poor for hydrazine. Nevertheless, such linear correlations might be useful for gases and liquids of low dipole moments and simple molecular structures.

Acknowledgment. The authors wish to express their appreciation for the assistance of Charles D. Robison of Aerospace Corporation in the construction of the apparatus.

(6) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1950, p 243.

(7) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

(8) The method of correlation was first used by J. E. Jolly and J. H. Hildebrand, *J. Am. Chem. Soc.*, **80**, 1050 (1958). Numerous examples are given in J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962. For a recent paper, see J. K. Dymond, *J. Phys. Chem.*, **71**, 1829 (1967).