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Thermodynamic Properties of Gases in Propellants

Solubility of He, N_2, and Ar in Hydrazine, Methylhydrazine, and Unsymmetrical Dimethylhydrazine

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Prepared by E. T. CHANG, N. A. GOKCEN, and T. M. POSTON
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Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04695-67-C-0158.

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Approved

R. A. Hartunian

R. A. Hartunian, Director
Aerodynamics and Propulsion
Research Laboratory

Pulication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Keith S Peyton

Keith S. Peyton, Capt, USAF
Project Officer

ABSTRACT

Solubilities of He, N_2, 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, N_2, 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 mol fractions of solutes in methylhydrazine and in unsymmetrical dimethylhydrazine but not of solutes in hydrazine.

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I. INTRODUCTION

Overcoming practical difficulties in pressurizing, storing, and pumping liquid propellants requires 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 (Ref. 1) dealt with the solubilities of He, N_2, O_2, Ar, and N_2O_3 in liquid N_2O_4. This paper reports the second part of the investigation, which deals with the solubilities of He, N_2, and Ar in liquid hydrazine, methylhydrazine (MH), and unsymmetrical dimethylhydrazine (UDMH).

None of the usual reference sources (Refs. 2 - 4) contain data on the solubilities in these binary gas-liquid systems. In addition, supplementary data, such as the values of density and vapor pressure for each liquid at various temperatures (Refs. 2-4) 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.

II. EXPERIMENTAL

The apparatus for solubility measurements was described in Ref. 1. Briefly, it consisted of three calibrated volumes for the measurements of admitted gases, a container in which the propellant 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 in detail in Ref. 5:

$$\rho(N_2H_4) = 1.02492 - 0.000565t \tag{1}$$

$$\rho(\mathrm{MH}) = 0.89338 - 0.000943t \tag{2}$$

$$\rho(\mathrm{UDMH}) = 0.80980 - 0.001030t \tag{3}$$

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 by violently stirring the liquid. The 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 described in Ref. 1 because the vapor pressure of MH and UDMH changes with time. These propellants, in an initially distilled pure state, dissociate slightly to yield increasing observed vapor pressure irrespective of the history of their treatment, subsequent methods of handling, or 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.

III. RESULTS

The results on the solubilities of He, N_2, and Ar in hydrazine, MH and UDMH are listed in Table I. Since the mol 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 fact is substantiated by the measurements at various pressures, and, further, it shows that there are no chemical reactions between nitrogen and the solvents (Ref. 1). The process of dissolution may be represented by

$$\text{Gas} \rightarrow \text{Dissolved Gas} \quad , \quad K = X/P \tag{4}$$

where X is the mol 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 values (Ref. 1) for He in N_2O_4.

The average values of K for the gases in hydrazine are represented in Fig. 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 $\Delta G°$ of Reaction (4) by $\Delta G° = -RT \ln K$, and are represented by

$$\Delta G°(\text{He in } N_2H_4) = 1,257 + 19.95T \tag{5}$$

$$\Delta G°(N_2 \text{ in } N_2H_4) = 2,364 + 15.59T \tag{6}$$

$$\Delta G°(\text{Ar in } N_2H_4) = 2,038 + 15.62T \tag{7}$$

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

Table I. Solubilities of He, N_2 and Ar in N_2H_4, MH, and UDMH

		He				N_2				Ar			
	T, °K	P, atm	10^5X		10^5K	P, atm	10^5X		10^5K	P, atm	10^5X		10^5K
N_2H_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				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
						2.0619	1.51		0.73				
								Av	0.69				
	308.18	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			Av	0.82			Av	1.39
		2.3070	1.44		0.62								
				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		[illegible]	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
UDMH	253.05	1.1719	5.83		4.97	1.2330	36.64		29.71	[illegible]	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
	273.15	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
								Av	32.7				
	293.16	1.4394	12.53		8.70	1.1587	42.70		36.85	0.9585	65.84		68.69
		2.2158	19.81		8.94	1.9521	71.30		37.04	1.7669	121.5		68.75
				Av	8.82			Av	36.9			Av	68.7

X = mol fraction; K = $\frac{X}{P}$

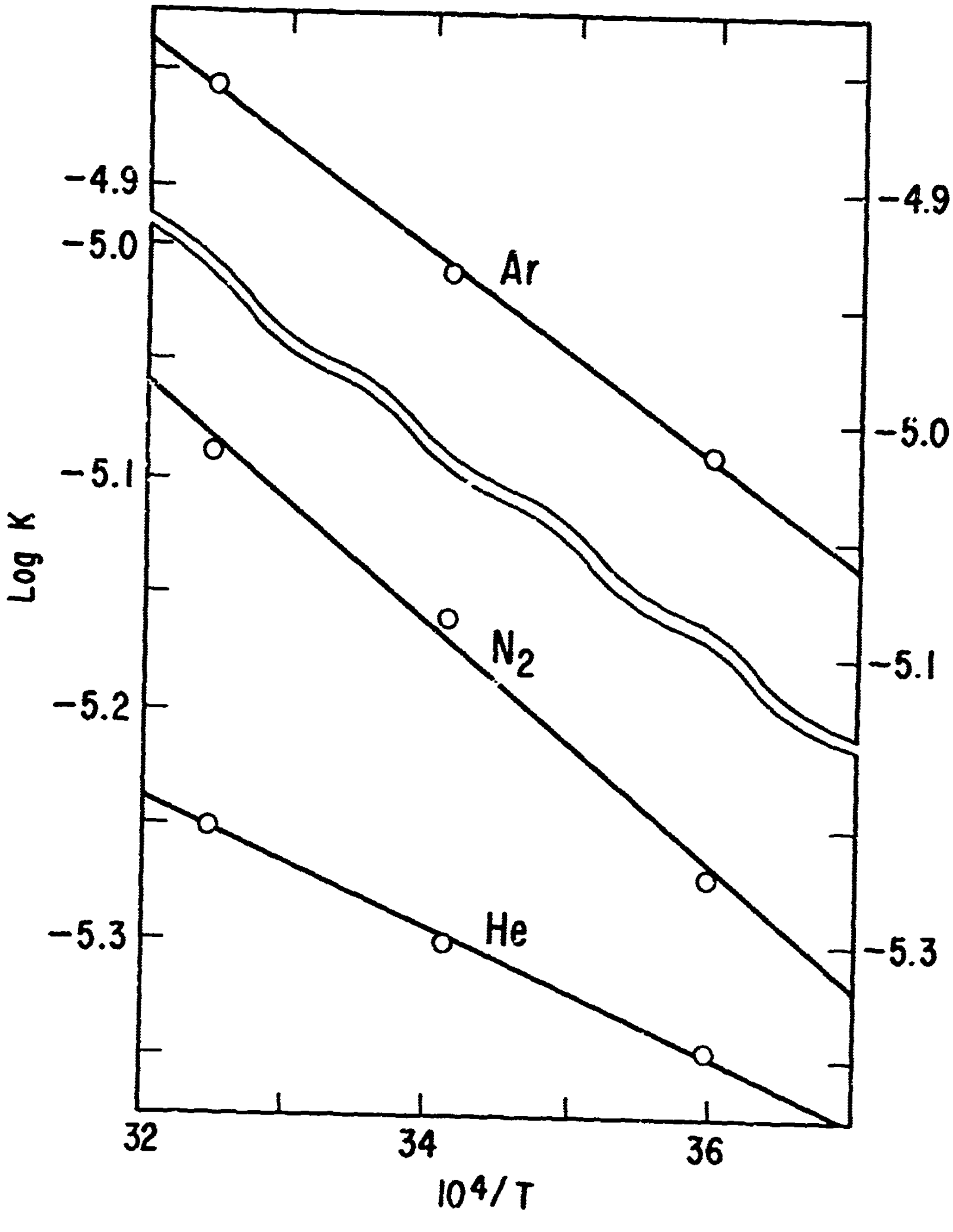

Fig. 1. Solubilities of He, N_2 and Ar in Liquid N_2H_4

The average values of K at each temperature for the gases in MH (Fig. 2) are expressed by

$$\Delta G^\circ(\text{He in MH}) = 1,798 + 15.02T \tag{8}$$

$$\Delta G^\circ(\text{N}_2 \text{ in MH}) = 1,118 + 14.72T \tag{9}$$

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

Similar data for the gases in UDMH, shown in Fig. 3, yield

$$\Delta G^\circ(\text{He in UDMH}) = 2,106 + 11.37T \tag{11}$$

$$\Delta G^\circ(\text{N}_2 \text{ in UDMH}) = 802 + 12.99T \tag{12}$$

$$\Delta G^\circ(\text{Ar in UDMH}) = 242 + 13.66T \tag{13}$$

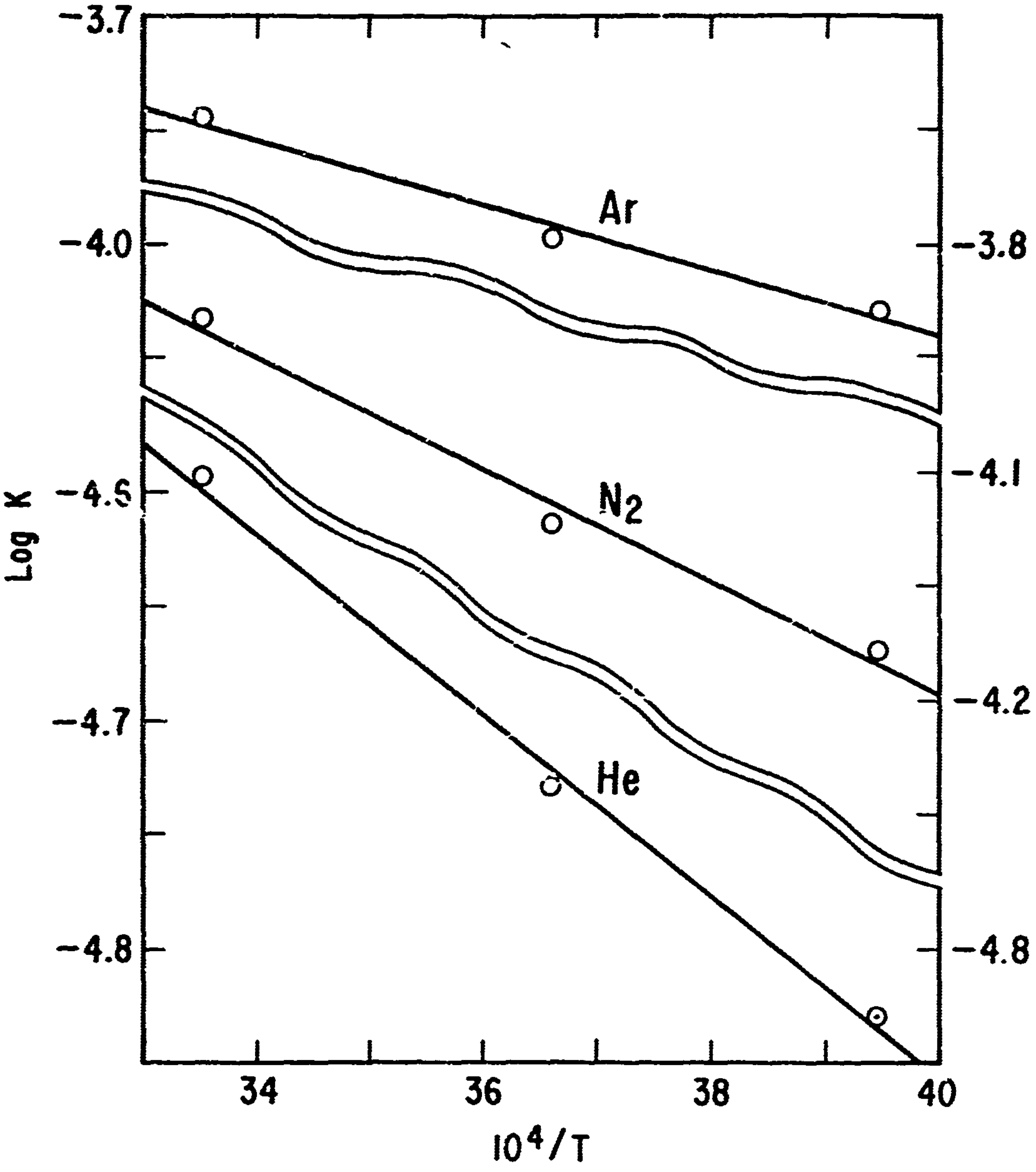

Fig. 2. Solubilities of He, N_2, and Ar in Liquid Methylhydrazine

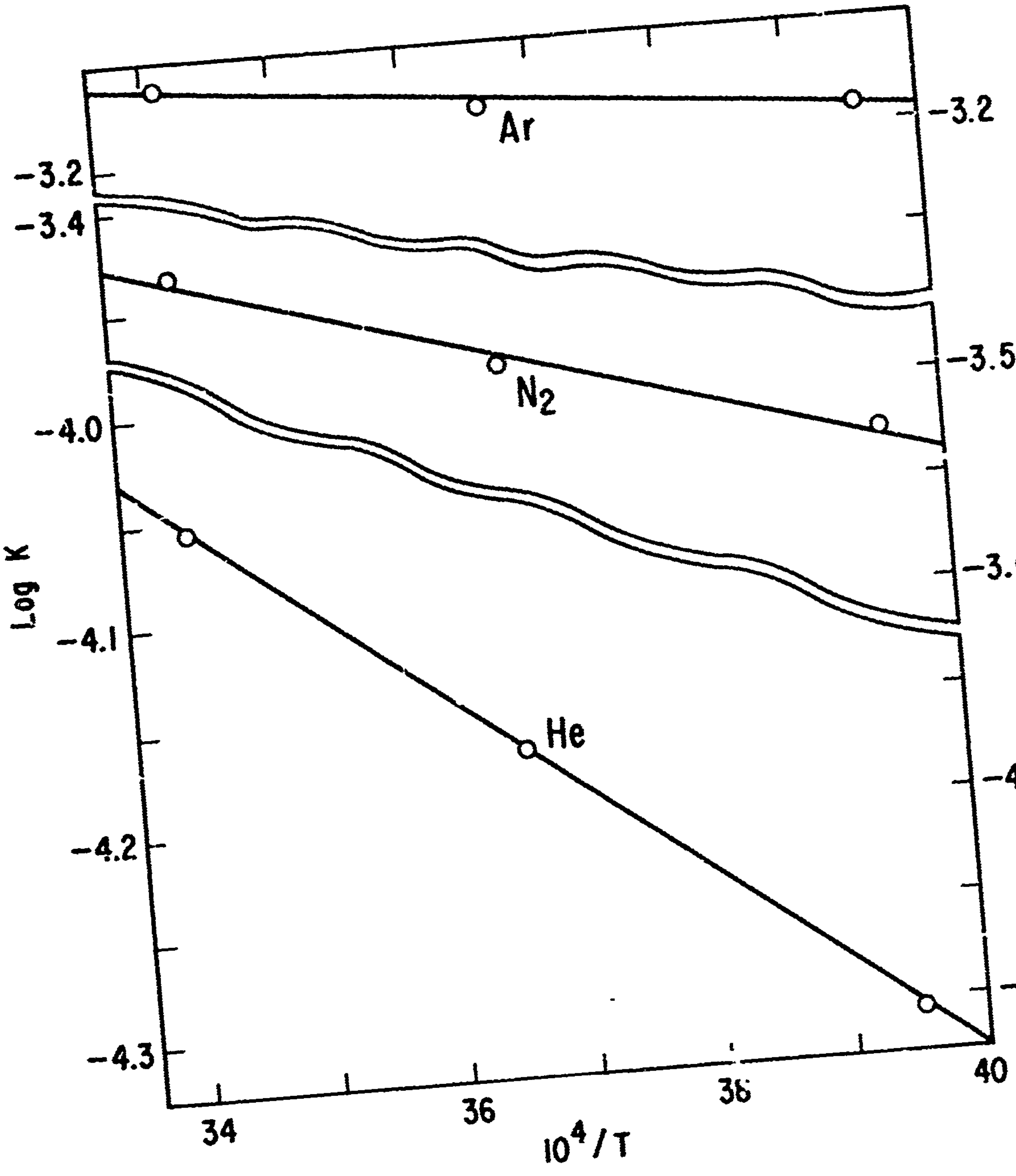

Fig. 3. Solubilities of He, N_2, and Ar in Unsymmetrical Dimethylhydrazine

IV. DISCUSSION

The process of dissolution of N_2 in all the propellants is that shown by Reaction (4) for 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 Eqs. (5-13) are of comparable magnitude and follow a pattern of variation from one gas to another. Hence, N_2 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 molecular or geometrically abstract models (Ref. 6) because, first of all, the molecules of the methyl hydrazines are complex and, further, the molecular parameters necessary for such treatments are not known. Therefore, we shall be satisifed with a reasonable semi-theoretical 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 potential (Ref. 7), in which the term involving $1/r^6$ is neglected, so that

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

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

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

(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 the 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 D of the solvent molecule. The value of D was obtained from the volume of the molecule, without considering the outer hydrogen atoms. This volume was converted into a sphere whose radius was taken to be identical with D. In essence, the sphere of radius 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 the hydrogen atoms. The results at $T_r = 1.11$ are presented in Fig. 4. The correlation is linear and supports our assumptions.

It is now possible to estimate ΔG° for the solubilities of He, N_2, and Ar in symmetrical dimethylhydrazine (SDMH) from the linear correlation in Fig. 4. For this purpose, it is also necessary to plot ΔG° versus r^{-12} at $T_r = 1.30$. The point where r^{-12} for SDMH (the vertical dotted line in Fig. 4) intersects 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 yield ΔG° as a linear function of temperature T in °K. The results are

$$\Delta G^\circ(\text{He in SDMH}) = 2,490 + 7.70T \tag{16}$$

$$\Delta G^\circ(N_2 \text{ in SDMH}) = 1,300 + 8.51T \tag{17}$$

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

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

The ideal or Raoultian solubility of He, N_2, and Ar in a liquid exhibiting no interaction with the solute gas is computed by calculating the vapor pressure P_i^v of a hypothetically existing gas and setting the mol fraction X_i equal to $1/P_i^v$, where 1 in the numerator is the atmospheric

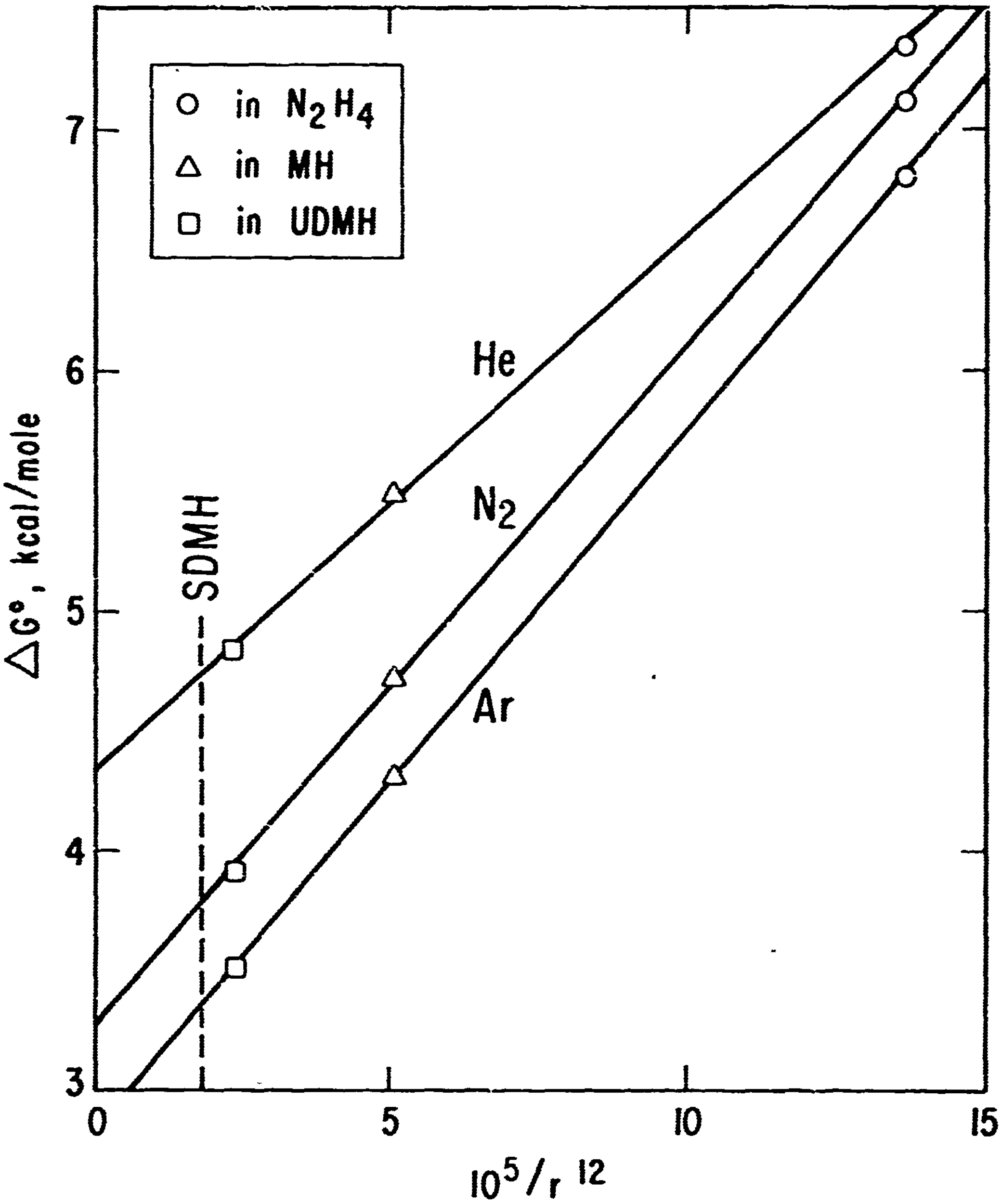

Fig. 4. Variation of Standard Change in Gibbs Energy of Solution $\Delta G°$ with Distance of Approach r of Solute and Solvent Molecules at $T = 1.11\ T_m$ (T_m = melting point, °K)

pressure. The results, taken from Hildebrand and Scott (Ref. 8), are shown in Table II, together with other data on solubilities and dipole moments μ (Ref. 9). 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 the 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 pattern (Ref. 6) shown in Table II, i.e., the solubilities increase with μ, although there are notable exceptions.

It has been shown by Hildebrand, et al. (Refs. 10-12), that when the entropy of solution, $\bar{S}$ (in soln) - S (gas) (where $\bar{S}$ is the partial molar entropy of dissolved gas in the solvent) for various gases is plotted versus the logarithm of mol fraction of solute at 1 atm, then a straight line results for each solvent at a chosen temperature. This correlation is very good for MH and UDMH, fair for the gases (Ref. 1) 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.

Table II. Comparison of Solubilities of He, N and Ar In Various Solvents at 25°C and 1 atm[a]

Solvent	μ, D	He	N_2	Ar
Ideal	. . .	16[b]	100	160
Hydrazine[b]	1.9[c]	0.52	0.72	1.24
Water	1.9	0.7	1.2	2.5
MH[b]	2.2[c]	2.51	9.17	17.9
UDMH[b]	2.5[c]	9.38	37.5	68.9
Acetone	2.8	10.8	59.2	90.6

[a] Numbers represent mol fraction $\times 10^5$.

[b] Authors' values of solubility.

[c] Dipole moments are from McClellan (Ref. 9); the value for $UDMH_2$ has been estimated by the authors from a plot of boiling point vs μ^2.

All the remaining data are from Hildebrand and Scott (Ref. 8).

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13. ABSTRACT

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