Table IV. Smoothed Values of Enthalpy for Mixture of 49.1 Wt % *cis*-2-Pentene and 50.9 Wt % *n*-Pentane

Units: Btu/lb. Base level: Pure saturated liquid components at −200°F

Temp, °F	Psia 0	300	400	450	500	515	600	700	800	1000	1400
350	416.6	392.1	306.9				305.0		303.1	301.9	300.7
360	421.9	398.6	315.1				313.2		311.5	310.0	308.0
360.4			315.6[a]								
365			387.2[a]								
370	427.1	405.1	391.5	324.1			321.7		319.9	318.1	315.3
375.8				329.9[a]							
377.8				385.1[a]							
380	432.4	411.6	399.6	388.5	334.4		330.7		328.2	326.0	322.5
386.6					343.2[a]						
389					378.2[a]						
390	438.0	418.1	407.2	400.1	382.1	350.6	340.4		336.5	334.0	330.2
391.6						361.3[b]					
391.9						374.3[c]					
395	440.7	421.2	411.1	405.0	392.2	386.0	345.8	342.2	340.7	338.0	333.9
400	443.3	424.6	415.0	409.2	399.0	394.5	352.0	347.7	345.0	341.8	337.6
410	449.1	431.1	422.0	417.4	409.1	405.9	375.8	359.3	354.1	350.2	345.7
420	454.8	437.9	429.1	424.3	417.9	415.0	398.0	371.9	364.2	359.3	353.9
430	460.7	444.4	436.0		425.5	423.5	410.7	388.0	375.3	367.9	361.8
440	466.6	451.1	443.0		433.2	431.2	420.8	403.0	387.1	376.5	370.1

[a] Enthalpy value on two-phase boundary. [b] Enthalpy at critical point. [c] Enthalpy at cricondentherm.

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Thermodynamic Properties of Gases in Propellants

Solubilities of Gaseous NH_3, CO, CO_2, and SF_6

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Ordinary gases are generally used for blanketing and pressurizing liquid propellants. Absorption and desorption of these gases cause undesirable mechanical and hydrodynamic effects in space vehicles. A series of investigations was therefore carried out to measure the solubilities of He, N_2, O_2, Ar, and N_2O_3 in liquid N_2O_4; and He, N_2, and Ar in liquid hydrazine, methylhydrazines, and their mixtures (*1–3*). The present investigation is on the solubilities of $NH_3(g)$ in liquid hydrazine (N_2H_4), in methylhydrazine (MH; $N_2H_3CH_3$), and in unsymmetrical dimethylhydrazine [UDMH; 1,1-$N_2H_2(CH_3)_2$]; CO(g) in UDMH; $SF_6(g)$ in MH and in N_2O_4; and $CO_2(g)$ in N_2O_4.

There are no available data on these gas–liquid systems except on the NH_3–N_2H_4 system at very high concentrations of ammonia (*6*). A small amount of ammonia in N_2H_4 improves the performance of N_2H_4 in special engines, and CO and CO_2 are potential pressurization gases for UDMH and N_2O_4. Compounds of sulfur and fluorine, in particular SF_6, have electrophyllic properties in engines using MH and N_2O_4. An accurate investigation of these gas–liquid systems is therefore warranted.

EXPERIMENTAL

The apparatus and the method for measuring the solubilities of gases are described elsewhere in detail (*1, 4*). Briefly, the apparatus for solubility measurements consists of three calibrated volumes for measuring the amounts of gases, a container

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Solubilities of gases at various temperatures and pressures in the following gas–liquid systems have been investigated: NH_3–N_2H_4, NH_3–$N_2H_3CH_3$, NH_3-1,1-$N_2H_2(CH_3)_2$, CO-1,1-$N_2H_2(CH_3)_2$, SF_6–$N_2H_3CH_3$, SF_6–N_2O_4, and CO_2–N_2O_4. The first component is the dissolved gas or solute, and the second component is the propellant or solvent in each binary system. The solubilities of NH_3 were found to obey Henry's law in the range of about 0.0–0.15 mol fraction of NH_3. All other gases are much less soluble than NH_3 and obey Henry's law at all concentrations. The standard Gibbs energy of solution of each gas in each liquid has been expressed as a function of absolute temperature. The activities of NH_3 and N_2H_4 in the system NH_3–N_2H_4 for the entire composition range have been calculated, and molecular interpretations for deviations from ideality are presented.

for the propellant stirred with a glass-enclosed magnet-bar, and a precision mercury manometer for measuring the pressure with a microslide cathetometer. The apparatus was all-Pyrex glass construction with short capillary connecting tubes joined by fusion. There are two capillary stopcocks sparingly lubricated with silicone grease and two Teflon O-ring joints.

The three volumes calibrated to ±0.0003 ml, were interconnected with short capillary necks, each with a calibration mark. These volumes were immersed in a thermostat whose temperature was nearly the same as the thermostated room controlled to ±0.1° where the apparatus was located. The volumes of all connecting tubes were also calibrated to the same precision. The pressure measurements were made with a barometer accurate to ±0.02 mm, and the manometer readings were read to ±0.01 mm with a micrometer slide-type cathetometer. The propellant bulb, with a capacity of about 100 ml, was calibrated with an accuracy of ±0.0002 ml by using water or mercury and was immersed in a thermostat controlled to ±0.01°C during the measurements.

The propellants had the following purity: N_2H_4, MH, and UDMH of 99% purity were further purified by double vacuum distillation; research grade N_2O_4 of 99.5% minimum purity was oxidized to remove a trace of N_2O_3 by bubbling oxygen, degassed under vacuum, and then distilled. The research grade gases, NH_3, CO, and CO_2 were of 99.99, 99.8, and 99.995% minimum purity, respectively. Sulfur hexafluoride, SF_6, initially 98.7% pure was purified by freezing in liquid nitrogen and evacuating to remove 1.1% air.

The volume occupied by the liquid was obtained by highly precise density measurements (*1*, *3*). The gas and the liquid were brought to equilibrium at a constant temperature by vigorously stirring the liquid. The amount of dissolved gas was found by subtracting the remaining gas from the initially admitted gas. The experimental procedure was checked for the solubility of nitrogen in water, and the result agreed within 2% of published data. The maximum error in all measurements was 2% of all solubilities reported in this paper.

RESULTS AND DISCUSSION

Ammonia in Propellants. The results for the solubility of ammonia in liquid N_2H_4, MH, and UDMH are listed in Table I and show that in the range of about 0–0.15 mole fraction of NH_3, Henry's law is obeyed—i.e., the solubility of gas in mole fraction X is proportional to the fugacity, f, of the gas. The fugacity of ammonia, f, in the pressure range of interest, the compressibility factor, Z, and the pressure, P, are related by

$$f = ZP \tag{1}$$

where Z is calculated from the pressure-volume-temperature data summarized by Din (*5*). The proportionality between X and f is shown in the lower left corner of Figure 1 where f is plotted vs. X for NH_3 in N_2H_4; similar plots may be drawn for NH_3 in MH and UDMH by using Table I. The slope in each such plot is the equilibrium constant K for the following reaction

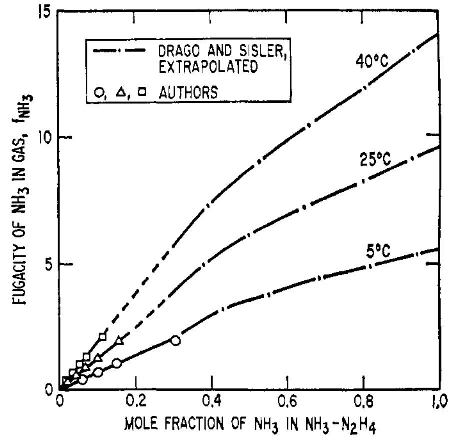

Figure 1. Fugacity of NH_3 over NH_3–N_2H_4 system

Extrapolation range is 88.5–124.9°C. Short dashed lines join sets of data

$$\text{Gas at } f \text{ atm} = \text{dissolved gas at } X \tag{2}$$

The constant K is given by

$$K = \frac{X}{f} \tag{3}$$

where f is in atmospheres, and K is in mole fraction per atmosphere. At sufficiently low pressures—i.e., less than 0.5 atm of NH_3—f approaches P, and K approaches K' of the following equation:

$$K' = \frac{X}{P} \tag{4}$$

The deviation from Henry's law is noticeably large above $f = 1$ in NH_3–N_2H_4 and NH_3–UDMH systems. The range of ammonia concentration in MH for the pressure range of interest is not large enough to show a measurable deviation from Henry's law. The thermodynamic equation representing K as a function of temperature T, in °K, is given by

$$\Delta G^\circ = -4.5756\, T \log K = \Delta H^\circ - T\, \Delta S^\circ \tag{5}$$

where ΔG°, ΔH°, and ΔS° are the standard Gibbs energy, enthalpy, and entropy of solution, respectively, for Reaction 2. The linear relationships represented by Equation 5 for the three gas–liquid systems are shown in Figure 2 where each point represents the average of all values of K at each temperature

Table I. Solubilities of NH_8 in N_2H_4, MH, and UDMH

	T, °K	P, atm	f, atm[a]	X	K'	K
N_2H_4	278.12	0.3857	0.3836	0.0556	0.1442	0.1449
		0.6818	0.6754	0.1003	0.1471	0.1485
		1.0351	1.0205	0.1481	0.1431	0.1451
		1.9597	1.9072	0.3058	0.1560	0.1603[b]
						Av 0.1462
	298.16	0.2812	0.2804	0.0218	0.0775	0.0777
		0.5695	0.5663	0.0444	0.0780	0.0784
		0.8516	0.8445	0.0661	0.0776	0.0783
		1.2207	1.2062	0.0975	0.0799	0.0808
		1.9332	1.8967	0.1553	0.0803	0.0819[b]
						Av 0.0788
	313.22	0.3305	0.3296	0.0171	0.0517	0.0519
		0.6661	0.6626	0.0334	0.0501	0.0504
		1.0049	0.9966	0.0501	0.0499	0.0503
		1.3176	1.3039	0.0689	0.0523	0.0528
		2.1154	2.0802	0.1125	0.0532	0.0541[b]
						Av 0.0514
MH	253.17	0.1561	0.1556	0.0786	0.5035	0.5051
		0.2693	0.2677	0.1310	0.4864	0.4894
						Av 0.4973
	273.15	0.1825	0.1820	0.0424	0.2323	0.2330
		0.5266	0.5224	0.1157	0.2197	0.2215
						Av 0.2273
	293.14	0.3425	0.3413	0.0423	0.1235	0.1239
		0.6206	0.6165	0.0752	0.1212	0.1220
		1.0055	0.9948	0.1190	0.1183	0.1196
						Av 0.1218
UDMH	253.17	0.0752	0.0751	0.0320	0.4255	0.4261
		0.2328	0.2317	0.0973	0.4180	0.4199
		0.9413	0.9225	0.3315	0.3522	0.3593[b]
		1.5035	1.4556	0.6222	0.4138	0.4275[b]
						Av 0.4230
	273.15	0.3133	0.3119	0.0650	0.2075	0.2084
		0.4827	0.4792	0.0982	0.2034	0.2049
		1.1635	1.1432	0.2456	0.2111	0.2148[b]
		1.8406	1.7898	0.3963	0.2153	0.2214[b]
						Av 0.2067
	293.14	0.3336	0.3324	0.0363	0.1088	0.1092
		0.7237	0.7181	0.0786	0.1086	0.1095
		0.9594	0.9496	0.1042	0.1086	0.1097
		1.4999	1.4760	0.1662	0.1108	0.1226[b]
		2.1459	2.0971	0.2377	0.1108	0.1133[b]
						Av 0.1095

[a] f = fugacity = ZP; X = mole fraction; $K' = X/P$; $K = X/f$; $P = P\,(\text{total}) - P\,(\text{solvent})$. [b] Not included in averaging. High concentration of dissolved gas is beyond validity of Henry's Law. However, these data are plotted in Figure 1.

in the range of validity of Equation 3. The thermodynamic relationships for the linear plots in terms of $\Delta G°$ are as follows:

$$\Delta G°(NH_3 \text{ in } N_2H_4) = -5204 + 22.53\,T \tag{6}$$

$$\Delta G°(NH_3 \text{ in MH}) = -5196 + 21.93\,T \tag{7}$$

$$\Delta G°(NH_3 \text{ in UDMH}) = -4986 + 21.40\,T \tag{8}$$

The equations for $\Delta G°$ show that ammonia releases about the same amount of heat—i.e., $\Delta H° \approx -5000$ cal/mol when 1 mole of NH_3 is dissolved in these propellants. This is also true for the entropy of solution, $\Delta S° \approx -22$ cal/mol °K. The decreasing trend in the absolute values of $\Delta H°$ and $\Delta S°$ follows the increasing number of CH_3 radicals in the propellants and shows that the interacting forces between H atoms in NH_3 and H in N_2H_4 are stronger than those between H in NH_3 and H in CH_3 radicals in MH and UDMH.

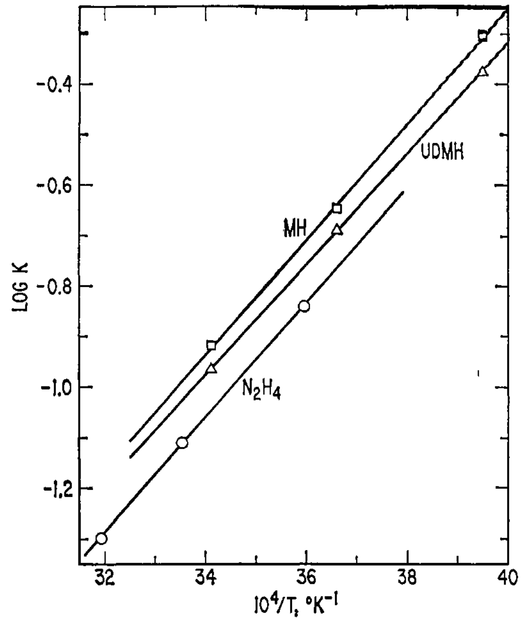

Figure 2. Variation of atmospheric solubility, K, with temperature for NH_3–N_2H_4, NH_3–MH, and NH_3–UDMH systems

The liquid-vapor equilibrium data for NH_3–N_2H_4 system have been obtained by Drago and Sisler (*6*) in the range of 0.30–0.95 mole fraction of NH_3 and 88.5–124.9°C. Their results are extrapolated from 88.5°C to lower temperatures by plotting the logarithm of fugacity of ammonia at a series of fixed compositions of liquid vs. $1/T$ in °K^{-1}. Such plots are the classical van't Hoff correlation in thermodynamics and extrapolate reliable data with confidence when scattering is extremely small. The resulting extrapolation correlates well with our data (Figure 1). The activity of NH_3, a_{NH_3}, which is defined by the fugacity of NH_3 over a given solution divided by the fugacity of NH_3 over pure liquid NH_3, obeys Henry's law and Raoult's law in their proper domains for large ranges of concentration. For example, a_{NH_3} at 25°C, is equal to its mole fraction in the range of about 0.6–1.00 mole fraction of NH_3 (Raoult's law), and a_{NH_3} is proportional to its mole fraction in the range of 0.0–0.15 mole fraction (Henry's law).

Activities in NH_3–N_2H_4 System. The activity of NH_3 from this investigation and from Drago and Sisler (*6*) has been calculated and listed in Table II. The calculation requires plotting $\log f_{NH_3}$ over each solution vs. $1/T$ to obtain an equation of $\log f$ as a linear function of $(1/T)$. When the linear function for $\log f_{NH_3}{}^*$ for pure liquid NH_3 is subtracted from $\log f_{NH_3}$, an equation for $\log (f/f^*) = \log a_{NH_3}$ is obtained

Table II. Thermodynamic Properties of NH_3 and N_2H_4 in Liquid NH_3–N_2H_4 System at 298.15 and 373.15°K

	NH_3[a]		N_2H_4		298.15°K		373.15°K	
X_{NH_3}	$\Delta\bar{H}$	$\Delta\bar{S}$	$\Delta\bar{H}$	$\Delta\bar{S}$	a_{NH_3}	$a_{N_2H_4}$	a_{NH_3}	$a_{N_2H_4}$
0.0			0.0	0.0	0.000	1.000	0.000	1.000
0.1	−1	4.01	−178	−0.39	0.133	0.902	0.163	0.958
0.2	−1	2.63	−178	−0.16	0.266	0.802	0.326	0.852
0.3	−1	1.83	−183	+0.09	0.398	0.701	0.398	0.746
0.4	+258	2.10	−298	+0.01	0.537	0.601	0.493	0.665
0.5	+400	2.19	−441	−0.13	0.653	0.508	0.570	0.590
0.6	+264	1.55	−267	+0.68	0.718	0.453	0.656	0.496
0.7	+150	1.02	−59	+1.65	0.773	0.395	0.734	0.403
0.8	+32	0.50	+295	+3.22	0.828	0.326	0.814	0.295
0.9	+127	0.56	+375	+4.62	0.931	0.184	0.905	0.162
1.0	0.0	0.0			1.000	0.000	1.000	0.000

[a] $\bar{H}$ is in cal/mol, and $\Delta\bar{S}$ is in cal/mol °K.

at the selected composition. The activity of ammonia is related to the Gibbs energy change by

$$\Delta\bar{G} = \Delta\bar{H} - T\,\Delta\bar{S} = RT \ln a_{NH_3} \qquad (9)$$

where $\Delta\bar{G}$ is defined by $\bar{G} - G^*$, $\bar{G}$ being the partial molar Gibbs energy of NH_3, and G^*, that of pure liquid ammonia. The changes in the partial molar enthalpy $\Delta\bar{H}$ and the entropy $\Delta\bar{S}$ are similarly defined. The values of $\Delta\bar{H}$ and $\Delta\bar{S}$ are listed in Table II. The activity coefficient of N_2H_4, $\gamma_{N_2H_4}$ has been calculated by graphical integration of the Gibbs-Duhem relationship $d \ln \gamma_{N_2H_4} = -(X_{NH_3}/X_{N_2H_4})\, d \ln \gamma_{NH_3}$. For this purpose, $X_{NH_3}/X_{N_2H_4}$ was plotted vs. $\ln \gamma_{NH_3}$, and the area under the curve was measured from $X_{N_2H_4} = 1.0$–0.1 at 0.1 intervals. The value of $\gamma_{N_2H_4}$ from $X_{N_2H_4} = 0.1$–0.0 is a constant in accordance with Henry's law. The results show that this system exhibits positive deviations from Raoult's, and the effect of temperature on the activity coefficients is small. The reason for this behavior stems from the fact that the interaction between the component molecules is through their *H* atoms which shield the *N* atoms. The two contacting *H* atoms, one from NH_3 and the other N_2H_4, are energetically in similar states and therefore repel each other slightly to cause small positive deviations from ideality.

The values of $\Delta\bar{H}$ and $\Delta\bar{S}$ for N_2H_4 are also listed in Table II. The values of $\Delta\bar{H}$ and $\Delta\bar{S}$ are small as expected from a small deviation from ideality. A slight irregularity in the pattern of variation for $\Delta\bar{H}$ is not serious because a small degree of scattering in the experimental data is ample to account for the scatter.

CO in UDMH and SF_6 in MH. The solubilities of CO in UDMH and SF_6 in MH are listed in Table III. Both gases obey Henry's law at all pressures at each temperature because the concentrations of dissolved gases are small. The values of *K* at each temperature are therefore constant, and a small scattering is simply due to the experimental errors. The logarithm of *K* is plotted vs. $1/T$ in °K^{-1} in Figure 3 wherein the relationship is linear. The equations for log *K* have been obtained as functions of $1/T$ by the least-squares method, and $\Delta G° = -4.5756\, T \log K$ has been used to derive the following equations:

$$\Delta G°(\text{CO in UDMH}) = 448 + 13.37\, T$$

$$\Delta G°(SF_6 \text{ in MH}) = -286 + 17.82\, T$$

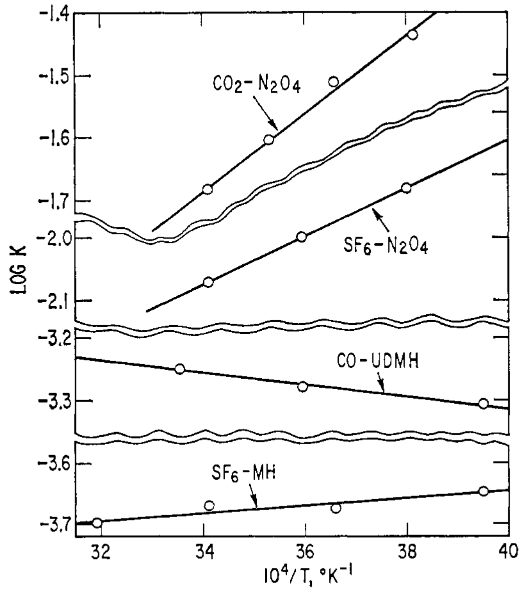

Figure 3. Variation of atmospheric solubility, *K*, with temperature for CO_2–N_2O_4, SF_6–N_2O_4, CO–UDMH, and SF_6–MH systems

Table III. Solubilities of CO in UDMH and SF_6 in MH

	T, °K	*P*, atm	*f*, atm[a]	10^4X	$10^4K'$	10^4K
CO in UDMH	253.24	0.9302	0.9293	4.62	4.97	4.97
		1.0190	1.0179	4.99	4.90	4.90
		1.5276	1.5252	7.60	4.98	4.98
		1.7539	1.7507	8.60	4.90	4.91
						Av 4.94
	278.13	0.8772	0.8767	4.59	5.23	5.24
		1.0861	1.0854	5.70	5.25	5.25
		1.6077	1.6061	8.46	5.26	5.27
		1.8643	1.8622	9.80	5.26	5.26
						Av 5.26
	298.16	1.0391	1.0387	5.86	5.64	5.64
		1.4056	1.4049	7.95	5.66	5.66
		1.8454	1.8442	10.46	5.67	5.67
		2.1012	2.0997	11.89	5.66	5.66
						Av 5.66
SF_6 in MH	253.17	0.2337	0.2326	0.52	2.23	2.24
		0.3233	0.3212	0.72	2.23	2.24
		0.9890	0.9692	2.18	2.20	2.25
		1.0524	1.0299	2.32	2.20	2.25
		1.9580	1.8802	4.28	2.18	2.27
		2.0329	1.9490	4.44	2.18	2.28
						Av 2.26
	273.15	0.5344	0.5299	1.11	2.08	2.09
		0.7783	0.7687	1.61	2.07	2.09
		0.8072	0.7969	1.69	2.09	2.12
		1.0920	1.0731	2.28	2.09	2.12
		1.9985	1.9352	4.13	2.07	2.13
		2.0802	2.0117	4.29	2.06	2.13
						Av 2.11
	293.14	0.7206	0.7141	1.50	2.08	2.10
		1.0085	0.9957	2.11	2.09	2.12
		1.0815	1.0668	2.24	2.07	2.10
		1.0955	1.0804	2.27	2.07	2.10
		1.9515	1.9037	4.16	2.13	2.19
		1.9557	1.9077	4.06	2.08	2.13
		2.1767	2.1173	4.48	2.06	2.12
						Av 2.12
	313.23	0.9514	0.9423	1.85	1.94	1.96
		1.7330	1.7028	3.47	2.00	2.04
						Av 2.00

[a] $f = ZP$ = fugacity; X = mole fraction; $K' = X/P$; $K = X/f$. Z for CO is from Hilsenrath *et al.* (*8*), and Z for SF_6 is calculated by using the Berthelot equation of state (*9*).

$\Delta G°$ for CO in UDMH is similar to N_2 and Ar in UDMH, and in fact $\Delta S°$ is about −13 for all three gases in UDMH (*3*).

CO_2 and SF_6 in N_2O_4. The solubilities of CO_2 and SF_6 in N_2O_4 are summarized in Table IV and represented in Figure 3. The corresponding equations for $\Delta G°$ are as follows:

$$\Delta G°(CO_2 \text{ in } N_2O_4) = -2{,}828 + 17.33\, T$$

$$\Delta G°(SF_6 \text{ in } N_2O_4) = -1{,}748 + 15.44\, T$$

The values of $\Delta H°$ are strongly negative in both systems because CO_2 and SF_6 do not break up the NO_2—NO_2 bond in N_2O_4 as He, Ar, N_2, and O_2 in N_2O_4 (*1*). The solubility of CO_2 in N_2O_4 is close to the ideal solubility at 1 atm computed from $X(CO_2) = 1/f°$, where $f°$ is the fugacity of pure liquid CO_2 at the temperature of interest, and *X* is the mole fraction. For example, the ideal solubility at 0°C is 0.0257 mole fraction (*7*), and the actual solubility is 0.0307 mole fraction as shown in Table IV. It is not surprising that CO_2–N_2O_4 are close to ideality since both CO_2 and N_2O_4 are anhydrous acidic compounds.

Table IV. Solubilities of CO_2 and SF_6 in N_2O_4

	T, °K	p, atm	f, atm[a]	10^3X	$10^3K'$	10^3K
CO_2 in N_2O_4	262.15	0.5773	0.5746	21.03	36.43	36.60
	273.15	0.1700	0.1698	5.276	31.04	31.07
		0.3366	0.3358	10.18	30.24	30.32
						Av 30.70
	283.20	0.3495	0.3488	8.712	24.93	24.98
		0.6690	0.6663	16.42	24.54	24.65
						Av 24.82
	293.15	0.1763	0.1761	3.742	21.23	21.25
		0.3175	0.3169	6.524	20.55	20.59
		0.6225	0.6203	12.65	20.32	20.39
						Av 20.74
SF_6-N_2O_4	263.15	0.7095	0.7005	8.179	11.53	11.68
		1.3778	1.3439	16.48	11.96	12.26
						Av 11.97
	278.13	0.6635	0.6570	6.427	9.687	9.782
		1.3957	1.3667	13.96	10.00	10.214
						Av 9.998
	293.14	0.4394	0.4370	3.643	8.291	8.336
		0.9478	0.9365	8.013	8.454	8.556
		1.1006	1.0854	9.346	8.492	8.611
						Av 8.501

[a] $f = ZP$ = fugacity; X = mole fraction; $K' = X/P$; $K = X/f$. Z for CO_2 has been taken from Hilsenrath et al. (*8*).

The solubilities of CO_2 in N_2O_4 and CO in UDMH are small enough to permit the use of these gases as pressurants in the low cost boosters. The solubility of SF_6 is small in MH but large enough in N_2O_4 to permit the use of this gas as an electrophyllic substance.

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Vapor Pressures and Second Virial Coefficients of Some Five-Membered Heterocyclic Derivatives

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Vapor pressures and second virial coefficients of furan, thiophene, pyrrole, and some of their substituted derivatives were measured by an isoteniscopic method in the temperature range 60–100°C.

Knowledge of vapor pressures and virial coefficients is necessary for the study of molecular interactions in systems involving a vapor phase—homogeneous gas phases or heterogeneous liquid-vapor systems. Especially gas-liquid chromatography allows the determination of activity coefficients γ_i of volatile solutes in the liquid stationary phase, from the well-known relationship:

$$V_g = \frac{273\,R}{f_i^0 \gamma_i^0 M} \tag{1}$$

where V_g is the specific retention volume of the compound i, f_i^0 is its vapor fugacity at the column temperature, and M is the molecular weight of the stationary phase.

When helium is used as the carrier gas, the interactions between the vapor of the solute i and this carrier gas can be neglected, and the fugacity f_i^0 is related to the vapor pressure P_i^0 and to the second virial coefficient B_{ii} by the equation:

$$\ln f_i^0 = \ln P_i^0 + \frac{P_i^0}{RT}(B_{ii} - v_i^0) \tag{2}$$

where v_i^0 is the molar volume of the pure liquid compound i. The derivation of these equations and the range of validity were discussed previously (*1, 2*).

The following measurements were performed with the aim of calculating the activity coefficients γ_i from chromatographic retention data using Equation 1. Since the values of P_i^0 and B_{ii} thus obtained were of more general use, it seemed useful to publish these data independently of any application.

EXPERIMENTAL

Measurements were made by the isoteniscopic method with the apparatus shown in Figure 1. The flask (A) containing the investigated compound and the null manometer (B) were immersed in a thermostated oil bath. The pressure measurements were made with the external manometer (C). Metallic contacts (m) and an electrovalve (D) permitted regulation of the mercury levels in the null manometer when the pressure in A approached equilibrium.

The investigated compound was introduced in the flask (A) through the Torion valve (E) (Prolabo, Paris, France) with a

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