713. *Dissociation of Liquid Dinitrogen Tetroxide; Henry's Law Coefficients, Heats and Entropies of Solution, and the Thermodynamics of Homolytic Dissociation in the Pure Liquid.*

By Peter Gray and P. Rathbone.

Existing measurements of the extent of dissociation in gaseous "nitrogen dioxide" ($NO_2 + N_2O_4$ equilibrium mixture) and of saturation vapour pressure and density of the pure liquid have been correlated and combined with optical densities for both gas and liquid to calculate the extent of dissociation in the liquid. Corrections have been made for deviations from ideal-gas behaviour and thermodynamic consistency has been tested throughout.

The composition of the liquid has been determined from the freezing point (triple point, −11·2° c) to the normal boiling point (21·15°). Throughout this range, dissociation is far less in the liquid than in the gas, so the liquid can be regarded as a very dilute solution of nitrogen dioxide in dinitrogen tetroxide and, on this basis, values determined for the Henry's law coefficients of NO_2 in solvent N_2O_4 and for the (hypothetical) vapour pressure of pure liquid N_2O_4. On the same basis, standard free energy, entropy, and enthalpy changes for the dissociation $N_2O_4 \rightleftharpoons 2NO_2$ in the pure liquid can be obtained. In solvent properties (both toward gaseous NO_2 and as a medium for its own dissociation) liquid dinitrogen tetroxide is not anomalous but takes its place among other solvents, such as benzene, carbon tetrachloride, chloroform, and carbon disulphide, in which the dissociation has been examined.

Dinitrogen tetroxide dissociates reversibly in the gaseous phase, in the pure liquid, and in solution. When a solution of dinitrogen tetroxide in an inert solvent is in equilibrium with the vapour phase a number of equilibria are set up: phase equilibria between the solvent and its vapour, between dissolved and gaseous NO_2 and N_2O_4, and chemical equilibria between N_2O_4 and NO_2 in both the liquid and the gaseous phase (see diagram).

$$\begin{tikzcd}
\begin{array}{c}2NO_2\\ \text{Dissolved}\end{array} \arrow[r, leftrightarrow, "\text{Phase equilibrium}"] \arrow[d, leftrightharpoons, "\begin{array}{c}\text{Chemical}\\ \text{equilibrium}\end{array}"'] & 2NO_2\ \text{gaseous} \arrow[d, leftrightharpoons, "\begin{array}{c}\text{Chemical}\\ \text{equilibrium}\end{array}"] \\
\begin{array}{c}N_2O_4\\ \text{Dissolved}\end{array} \arrow[r, leftrightarrow, "\text{Phase equilibrium}"'] & N_2O_4\ \text{gaseous}
\end{tikzcd}$$

If a solution of dinitrogen tetroxide in the solvent is sufficiently dilute for the solvent to obey Raoult's law, then, by analysis of liquid and vapour phases, together with vapour-pressure measurements on the solution, it is possible to obtain Henry's law coefficients (k_1 and k_2) for the solutes NO_2 and N_2O_4 from the defining equations (symbols used are defined below):

$$\text{For } NO_2,\ k_1 \equiv \underset{x_1 \to 0}{\text{Lt}}\,(y_1P/x_1) \qquad \text{For } N_2O_4,\ k_2 \equiv \underset{x_2 \to 0}{\text{Lt}}\,(y_2P/x_2)$$

Atwood and Rollefson [1] calculated the Henry's law coefficients of NO_2 and N_2O_4 in carbon tetrachloride, and found $k_1 = 76$ atm. and $k_2 = 2{\cdot}5$ atm.

Hitherto it has been assumed that gaseous NO_2 and N_2O_4 behave ideally. However, in order to obtain accurate values for the Henry's law coefficients of NO_2 and N_2O_4, the experimental results must be corrected for gas imperfections (Appendix). In the saturated vapour, dinitrogen tetroxide is considerably dissociated; the degrees of dissociation at

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[1] Atwood and Rollefson, *J. Chem. Phys.*, 1941, **9**, 506.

the freezing point (−11·2°) and at the boiling point (+21·15°) are 8·6% and 15·9% respectively. However, in the liquid phase, homolytic dissociation is very much less (0·018% at the f. p. and 0·12% at the b. p.). The electrical conductivity [2] of the liquid is minute ($1{\cdot}26 \times 10^{-13}$ ohm^{-1} cm.$^{-1}$ at 0°; about that of kerosene) and thus the concentration of any ions in the liquid must be minute. Hence from the freezing to the boiling point both homolytic and heterolytic dissociation are stoicheiometrically negligible, and the liquid consists almost wholly of N_2O_4, so the liquid equilibrium mixture can be treated as a very dilute solution with N_2O_4 as solvent (and assumed to obey Raoult's law) and NO_2 as solute, and treated in terms of Henry's law:

(Partial pressure of NO_2) = (Henry's law coefficient of NO_2) × (Mole fraction of NO_2); $y_1P = k_1x_1$
(Partial pressure of N_2O_4) = (Hypothetical vapour pressure) × (Mole fraction of N_2O_4); $y_2P = P^0x_2$

From the knowledge of the Henry's law coefficient of NO_2 at different temperatures, the standard free energy of solution for each temperature, and the mean standard entropy and enthalpy of solution over the temperature range can be obtained. The combination of these results with accurate thermodynamic data [3] for gaseous equilibrium enables self-consistent thermochemistry for the dissociation in the liquid phase to be established. We now derive the Henry's law coefficient for NO_2 dissolved in N_2O_4 and the hypothetical vapour pressure of pure liquid N_2O_4 from −11·2° to +21·1°.

The calculations are based on measurements of vapour pressure [3] and of gaseous equilibrium constants (K_f),[3-8] together with optical densities [9-11] of both the gaseous and the liquid state. The composition of the vapour is found from the first two; the composition of the liquid from that of the vapour, together with the optical density of gaseous and liquid phases. Hence the Henry's law coefficient of NO_2 and hypothetical vapour pressure of N_2O_4 can be determined. Our treatment appears to be the first to assess the influence of gas imperfections, to specify standard states correctly, and to check consistency. The results differ significantly from previous ones.

We use the following symbols: c_1 and c_2 are the concentrations of NO_2 and N_2O_4 respectively in the gaseous phase, and c_1' and c_2' those in the liquid phase (moles/l.); ΔG° and ΔG_l^* are the standard free energy of dissociation of N_2O_4 in the gaseous and the liquid phase (cal./mole of N_2O_4), and ΔG_s^* the standard free energy of solution of gaseous NO_2 in liquid N_2O_4 to form an ideal dilute solution of NO_2 in N_2O_4 of unit activity (cal./mole of N_2O_4); ΔH_g and ΔH_l are the enthalpies of dissociation (cal./mole of N_2O_4) in the gaseous and the liquid phase; K_c and K_c' are equilibrium constants (moles/l.) in terms of concentration, and K_x and K_y in terms of mole fractions, in the liquid and the gaseous phase; K_f and K_p are equilibrium constants (atm.) in the gaseous phase in terms of fugacities and partial pressures; k is the Henry's law coefficient (atm.) of NO_2 in N_2O_4; L_e is the enthalpy of vaporisation of liquid equilibrium mixture (cal./mole of N_2O_4) at 21·15°/1 atm.; L_1 is the enthalpy of vaporisation of the same mixture (cal./mole of NO_2) to give pure gaseous N_2O_4 at 21·15°/1 atm.; L_1^* is the standard enthalpy of solution of gaseous NO_2 (cal./mole of NO_2) to form an infinitely dilute solution of NO_2 in N_2O_4 at 21·15°/1 atm.; L_2 is the enthalpy of vaporisation of liquid equilibrium mixture (cal./mole of N_2O_4) to give pure gaseous N_2O_4 at 21·15°/1 atm.; L_2° is the standard enthalpy of vaporisation (cal./mole of N_2O_4) of pure liquid N_2O_4 to give pure gaseous N_2O_4 at 21·15°/1 atm.; P is the vapour pressure (atm.) of the equilibrium mixture; P° is the hypothetical

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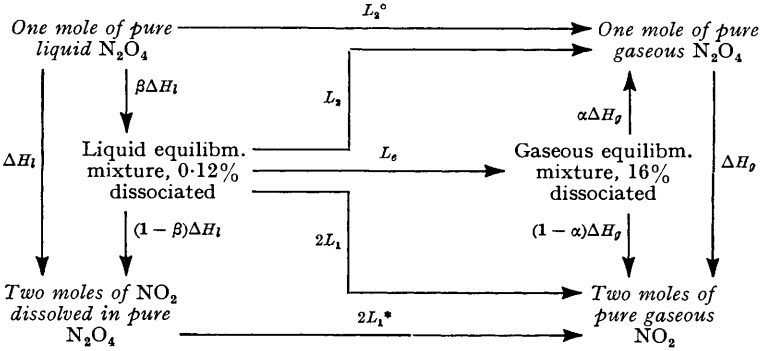
[2] Bradley, *Trans. Faraday Soc.*, 1956, **52**, 1255.
[3] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.
[4] Natanson and Natanson, *Ann. Physik*, (*a*) 1885, **24**, 454; (*b*) 1886, **27**, 606.
[5] Bodenstein and Boës, *Z. phys. Chem.*, 1922, **100**, 75.
[6] Wourtzel, *Compt. rend.*, 1919, **169**, 1397.
[7] Bodenstein and Katayama, *Z. phys. Chem.*, 1909, **69**, 26.
[8] Verhoek and Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250.
[9] Cundall, *J.*, (*a*) 1891, **59**, 1076; (*b*) 1895, **67**, 794.
[10] Steese and Whittaker, *J. Chem. Phys.*, 1956, **24**, 776; Whittaker, *ibid.*, p. 780.
[11] Hall and Blacet, *J. Chem. Phys.*, 1940, **24**, 1745.

vapour pressure of pure liquid N_2O_4; ΔS° and ΔS^* are the standard entropy of dissociation (cal./deg. per mole of N_2O_4) of N_2O_4 in the gaseous and the liquid phase; ΔS_s^* is the standard entropy of solution of gaseous NO_2 in liquid N_2O_4 (cal./deg. per mole of N_2O_4) to form an ideal dilute solution (unit activity) of NO_2 in N_2O_4; V_g and V_l are the volumes (cm.^{3}/mole) of gaseous and liquid equilibrium mixture per formula weight of N_2O_4; x_1 and x_2 are the mole fractions in the liquid, and y_1 and y_2 in the gaseous, phase for NO_2 and N_2O_4 respectively; α and β are the degrees of dissociation of N_2O_4 in the gaseous and the liquid phase; ε and ε' are the optical density per unit length (cm.$^{-1}$) in the gaseous and the liquid phase, and λ_1 and λ_2 the second virial coefficients (atm.$^{-1}$) of gaseous NO_2 and N_2O_4; ρ is the density of liquid N_2O_4 (g./cm.^{3}).

Reference States.—In the gaseous phase N_2O_4 is considerably dissociated, so the pure constituents NO_2 and N_2O_4 at unit pressure (1 atm.) are convenient reference states. However, although pure liquid N_2O_4 is a natural and convenient reference state, for liquid NO_2 a better reference is the hypothetical infinitely dilute solution in N_2O_4. The reference states employed here and their relations to one another and to experimentally realizable systems are displayed in the Scheme.

SCHEME. *Interrelations among reference states for liquid–vapour system. All magnitudes refer to* 92·016 *g.* (1 *formula wt.* N_2O_4) *at* 21·15°/1 *atm. Hypothetical standard states are in italics.*



Determination of Henry's Law Coefficient of NO_2 (*k*) *and the Hypothetical Vapour Pressure* (P°) *of the Pure* N_2O_4 *Species.*—The equations

$$k = y_1P/x_1 \qquad y_2P = x_2P^\circ$$

show that it is necessary to know the three quantities P, y_1, and x_1.

1. *Saturated vapour pressure P.* Giauque and Kemp [3] accurately measured the vapour pressure of the equilibrium mixture from $-32{\cdot}8^\circ$ to $+21{\cdot}8^\circ$, and gave an accurate empirical equation for the vapour pressure of the equilibrium mixture as a function of temperature:

$$\log_{10}P \text{ (internat. cm. Hg)} = 8{\cdot}00436 - 1753{\cdot}000/T - 1{\cdot}1807(T/1000) + 2{\cdot}094(T/1000)^2$$

This equation was used to give the vapour pressure of entry 1 in Table 1.

2. *Composition of the vapour.* The mole fractions (y_1 and y_2) in the gaseous phase can be obtained from vapour-pressure measurements and the gaseous equilibrium constant (K_f) through the equations

$$y_1^2P/y_2 \equiv K_p = K_f = \exp(-\Delta G^\circ/\boldsymbol{R}T) \qquad y_1 + y_2 = 1$$

To obtain the concentrations (c_1 and c_2) of each of the two species from the mole fractions requires correction for gas imperfection. The following equations (see Appendix) relate c and y:

$$c_1\boldsymbol{R}T = y_1P/(1 + \lambda_1P) \qquad c_2\boldsymbol{R}T = y_2P(1 + \lambda_2P)$$

Various determinations of K_p, from which K_f can be obtained, have been made. The conditions [4-8] were very varied, so that comparison of the results is difficult. Giauque and Kemp[3] correlated all the available experimental data and their correlation represents the best set of data for the gas-phase equilibrium. They tabulated their results as values of $\Delta[(G^\circ - H_0^\circ)/T]$, where $\Delta H_0^\circ = 12{,}875 \pm 16$ cal./mole of N_2O_4. By plotting this function against temperature we obtained its value at the desired temperature, and from this ΔG°. Hence, through K_f we obtained the mole fractions and concentrations in the gaseous phase (see entries 3 to 10 of Table 1: the equilibrium "constant" in terms of concentrations K_c for various temperatures is entry 11 and its logarithm is entry 12).

TABLE 1. *Saturation vapour pressures, equilibrium constants, and optical densities used to derive composition of liquid dinitrogen tetroxide. Entries* 26 *to* 33 *are mean values. For units see definition of symbols.*

	Temp. (°K)	261·9	263·1	273·1	283·1	293·1	294·2
1	P	0·1839	0·1973	0·3454	0·5822	0·9475	1·0000
2	$-\Delta\{(G^\circ - H_0^\circ)/T\}$	38·886	38·902	39·032	39·142	39·246	39·257
3	ΔG°	2692	2641	2215	1794	1372	1325
4	10^3K_f	5·657	6·390	16·92	41·16	94·75	103·6
5	10^3K_y	30·76	32·39	48·99	70·70	100·0	103·6
6	10^2y_1	16·07	16·48	19·82	23·29	27·02	27·42
7	10^2y_2	83·93	83·52	80·18	76·71	72·98	72·58
8	$-10^2\lambda_1$	0·707	0·698	0·624	0·560	0·505	0·499
9	10^3c_1	1·377	1·508	3·062	5·857	10·695	11·417
10	10^3c_2	7·202	7·655	12·41	19·35	29·03	30·37
11	10^4K_c	2·633	2·972	7·556	17·73	39·38	42·92
12	$\log_{10} K_c$	$\bar{4}$·4205	$\bar{4}$·4730	$\bar{4}$·8783	$\bar{3}$·2487	$\bar{3}$·5953	$\bar{3}$·6327
13	ε_{6130}	0·0174	0·0185	0·0340	0·0632	0·1095	0·1163
14	ε_{5920}	0·0278	0·0300	0·0538	0·1008	0·1743	0·1834
15	ε_{5760}	0·0184	0·0195	0·0323	0·565	0·1098	0·1176
16	ε_{6130}/c_1	12·6	12·3	11·1	10·8	10·2	10·2
17	ε_{5920}/c_1	20·2	19·9	17·6	17·2	16·3	16·1
18	ε_{5760}/c_1	13·4	12·9	10·6	9·65	10·3	10·3
19	ε'_{6130}	0·046	0·050	0·094	0·167	0·284	0·299
20	ε'_{5920}	0·077	0·083	0·148	0·264	0·440	0·464
21	ε'_{5760}	0·099	0·107	0·200	0·356	0·604	0·640
22	$10^3c_1'$ $\lambda = 6130$	4·14	4·51	8·47	15·1	25·6	26·9
23	$\lambda = 5920$	4·34	4·68	8·34	14·9	24·8	26·2
24	$\lambda = 5760$	9·17	9·91	18·5	33·0	55·9	59·3
25	ρ	1·517	1·515	1·492	1·469	1·446	1·447
26	10^4x_1	3·57	3·86	7·26	13·1	22·5	23·8
27	k	94·4	95·7	108	118	131	132
28	$\log_{10} k$	1·975	1·981	2·034	2·073	2·116	2·122
29	P°	0·1544	0·1648	0·2771	0·4472	0·6931	0·7275
30	$\log_{10} P^\circ$	$\bar{1}$·189	$\bar{1}$·217	$\bar{1}$·443	$\bar{1}$·650	$\bar{1}$·841	$\bar{1}$·862
31	10^8K_x	14·7	17·3	61·5	201	593	667
32	$10^6K_c'$	2·43	2·84	9·97	32·1	93·4	105
33	$\log_{10} K_c'$	$\bar{6}$·386	$\bar{6}$·453	$\bar{6}$·999	$\bar{5}$·507	$\bar{5}$·970	$\bar{4}$·021

3. *Composition of the liquid.* NO_2 is an odd-electron molecule and hence paramagnetic. It absorbs light over a wide range, and the colour of the gas and liquid is due to its presence. The diamagnetic dimer N_2O_4 is transparent over a wide range of wavelength. Both magnetic and optical properties have been used to investigate the equilibrium in the liquid (where pressure and density methods are inapplicable); optical methods are the more accurate.

Cundall first examined the dissociation of the pure liquid in bulk and in solution in various solvents, with a white-light colorimetric technique[9] over a considerable range of temperature. Steese and Whittaker[10] improved and extended his work. They measured the optical density of both the gaseous and the liquid phase from −10° to 20° with monochromatic light of three different wavelengths for which NO_2 absorbs and N_2O_4 does not. In Table 1 Steese and Whittaker's values, at different temperatures, of the absorption coefficients (ε_λ) for the saturated vapour are entries 13 to 15; the corresponding absorption coefficients (ε'_λ) for the liquid are entries 19 to 21.

If it is assumed that the ratio of the optical densities in the liquid and the vapour phase is equal to the ratio of concentrations then the composition of the liquid phase can be determined:

$$\text{Concentration of NO}_2\text{ in liquid} = \text{Optical density of liquid}/(\text{optical density of gas/concentration of NO}_2\text{ in gas})$$

From the known composition of the liquid, only densities are required to obtain the mole fractions x_1 and x_2 of NO_2 and N_2O_4 in the liquid phase.

For this assumption to be *exactly* true the ratio of the absorption coefficients ($\varepsilon'_\lambda/\varepsilon_\lambda$) must be completely independent of wavelength, temperature, and total pressure. These factors are now considered in more detail.

Wavelength. When a vapour is liquefied, both the intensity of optical absorption and the positions of the absorption maxima are altered. The most satisfactory comparisons of the absorption intensities are those based on the integrated intensities or peak-heights of *corresponding* maxima in the absorption spectra of the gaseous and the liquid phase respectively. When this comparison is not possible, it is best to derive values from absorption data at as many wavelengths as possible. This method was applied here to Steese and Whittaker's optical-density data for $\lambda = 6130$ Å, 5920 Å, and 5760 Å; hence the concentration of NO_2 in the liquid, at each particular temperature, can be expressed as the mean of three values.

Temperature. The absorption maxima also move with temperature (collision broadening), and to a slightly different extent for the liquid and the gaseous phase. Therefore, for any particular wavelength, the absorption coefficient in both the liquid and the gaseous phase will vary slightly with temperature, so the quotient (absorption coefficient in gaseous phase/concentration of NO_2), *i.e.*, (ε_λ/c_1), will show a definite trend with temperature, as seen from entries 16—18 of Table 1. The observations, however, are not accurate enough for this variation to be significant. At 6130 Å and 5920 Å (ε_λ/c_1) decreases with increase in temperature, and at 5760 Å has a minimum at about 10°. Mean values of (ε_λ/c_1) were used: at 6130 Å, 11·10; 5920 Å, 17·74; 5760 Å, 10·80. (The geometric mean was chosen since this corresponds to the arithmetic mean for the entropy and enthalpy of dissociation in the liquid phase.) This treatment uses the considerably greater accuracy with which the concentration of NO_2 in the gaseous phase is known. The value of the absorption coefficient in the liquid phase also depends on temperature, but the additional errors due to this are small because, first, it is the *ratio* of the optical densities which concerns the above calculations and, secondly, the temperature range is small ($-11°$ to $+21°$).

Pressure. The absorption coefficient in the liquid will be virtually unaffected by increase in pressure, owing to the very small effect of increase of pressure on a condensed phase. The absorption coefficient in the gas will vary more. However the pressure range is small and the total pressure never exceeds 1 atm. As Hall and Blacet[11] found that large pressures of nitrogen did not affect the absorption coefficient or the structure of the spectrum, pressure probably does not have any appreciable effect.

The Henry's law coefficient of NO_2 and the hypothetical vapour pressure of pure liquid N_2O_4 can now be calculated (entries 27 and 29 of Table 1).

DISCUSSION

The extent of dissociation is very much less in the liquid than in the gas phase. At the normal boiling point (21·15°/1 atm.), when the saturated vapour is 15·9% dissociated ($K_c = 4{\cdot}29 \times 10^{-3}$ mole/l.), the liquid is only 0·12% dissociated, ($K_c' = 1{\cdot}05 \times 10^{-4}$ mole/l.). Dissociation in the liquid decreases rapidly with falling temperature; it is 0·078% at 0° (K_c' is $1{\cdot}00 \times 10^{-5}$ mole/l.), and 0·038% at the triple point (−11·2°/0·184 atm.) (K_c' is $2{\cdot}43 \times 10^{-6}$ mole/l.).

The Henry's law coefficient for NO_2 dissolved in N_2O_4 varies from 94 atm. at the freezing point to 132 atm. at the boiling point. At 25° the extrapolated value is 136 atm.

This is larger than (although of the same order of magnitude as) the value for the Henry's law coefficient of NO_2 in carbon tetrachloride at 25° (76 atm.). Carbon dioxide and sulphur dioxide have been used as models by various workers in their assessment of imperfections of gaseous NO_2. For these gases in carbon tetrachloride the Henry's law coefficients are 100 and 14 atm. respectively.

When a gas (at 1 atm. pressure) forms an ideal solution in a liquid, then its Henry's law coefficient is equal to its liquefaction pressure at the temperature of the solution. If, in carbon tetrachloride, NO_2, carbon dioxide, and sulphur dioxide deviate from ideality to about the same extent, then the hypothetical liquefaction pressure of NO_2 can be estimated roughly as about 45 atm. at 25°.

The standard free energy (ΔG_s^*), entropy (ΔS_s^*), and enthalpy (L_1^*) of solution of NO_2 in solvent N_2O_4 are approximately related to the Henry's law coefficient by the equations:

$$\Delta G_s^* = \boldsymbol{R}T \ln k$$

$$\Delta S_s^* = -\,\mathrm{d}\Delta G_s^*/\mathrm{d}T = \boldsymbol{R}T\,\mathrm{d}\ln k/\mathrm{d}T - R\ln k, \text{ and}$$

$$L_1^* = \Delta G_s^* + T\Delta S_s^* = \boldsymbol{R}T^2\,\mathrm{d}\ln k/\mathrm{d}T$$

"Standard" and the superscript * denote changes from the dissolved state at a particular concentration (strictly, activity) to the gaseous state *at the same concentration.* Here, this concentration is 1 mole/l.

TABLE 2. *Thermodynamics of solution of* NO_2 *in* N_2O_4.

Temperature	−11·2°	−10°	0°	10°	20°	21·15°
ΔG_s^* (cal./mole of NO_2)	738	748	819	882	948	959

L_1^* (mean) = −1560 cal./mole of NO_2; ΔS_s^* (mean) = −8·60 cal./deg. per mole of NO_2.

TABLE 3. *Thermodynamics of the dissociation of* N_2O_4 *in the gaseous and the liquid phase and in various solvents at* 20°.

Solvent	$10^5K_c'$ (moles/l.)	ΔH_l^* (cal./mole)	ΔG_l^* (cal./mole)	ΔS_l^* [cal./(deg. mole)]	$10^6K_c'V$ (moles)
$SiCl_4$	17·8	20,500	5030	52·7	20·4
CS_2	13·3	19,400	5200	48·6	8·03
CCl_4	8·05	18,800	5490	45·6	7·76
$CHCl_3$	5·53	21,200	5710	52·9	4·41
C_2H_5Br	4·79	20,500	5790	50·2	3·65
C_6H_5Br	3·70	19,400	5940	45·8	4·35
C_6H_6	2·23	22,200	6240	54·4	1·98
Pure liquid	10·47	17,820	5300	43·0	5·84
Pure gas	394	13,693	32	35·7	—

Table 2 shows the values of these thermodynamic functions. The entropy of solution (−8·6 cal. per deg. per mole of NO_2) can be related to the free volume per mole of NO_2 in solution (V_f) since

$$\Delta S_s^*/\boldsymbol{R} \simeq \ln (V_f/V_g)$$

where V_g is the molar volume of NO_2 in the gaseous phase. An estimation of V_f by this method gave a result of 13 cm.^{3}/mole of NO_2 which may be compared with the geometrical volume at the same temperature of 32 cm.^{3}/mole of NO_2.

The equation which expresses enthalpy of solution of NO_2 in N_2O_4 (L_1^*) in terms of Henry's law coefficient (k) requires corrections for gas imperfections. This leads to the equation:

$$L_1^* = -\boldsymbol{R}T^2(1 + \lambda_1 P)(\mathrm{d}\ln k/\mathrm{d}T),$$

and to a value of $L_1^* = 1560 \pm 120$ cal./mole of NO_2 at the normal boiling point ($P = 1$ atm.). The data are not precise enough to reveal any significant variation with temperature.

Similarly the enthalpy of vaporization of N_2O_4, L_2°, can be obtained from the temperature dependence of the (hypothetical) vapour pressure, P°, of pure N_2O_4 since

$$L_2^\circ = (1 + \lambda_2 P)\,\boldsymbol{R}T^2\,(\mathrm{d}\ln P_0^\circ/\mathrm{d}T) = 7270 \pm 30 \text{ cal./mole of } N_2O_4 \text{ at normal b. p.}$$

This latent heat corresponds to a Trouton's "constant" of about 24·5 cal./deg. per mole of N_2O_4, which may be contrasted with the apparent Trouton's "constant" for the equilibrium mixture (L_e/T_b) which is abnormally increased to 31 cal./deg. per mole of N_2O_4 by the dissociation of gaseous N_2O_4.

Thermodynamic data for the dissociation of N_2O_4 in the gaseous state, in various solvents, and in the pure liquid, are in Table 3. The results obtained for liquid N_2O_4 lie among those for the other liquid solvents: dissociation is least in benzene ($K_c' = 2{\cdot}23 \times 10^{-5}$ mole/l.) and is greatest in silicon tetrachloride ($K_c' = 17{\cdot}8 \times 10^{-5}$ mole/l.); in all solvents dissociation is much less than in the gas phase ($K_c = 394 \times 10^{-5}$ mole/l.).

For an ideal solution the fraction (K_x/K_y) at a given temperature should be independent of the solvent, and in the case of an ideal *dilute* solution (K_c'/K_c) should depend only on the molar volume of the solvent; the product $K_c'V$ should be constant. Table 2 shows that this condition is not satisfied. There appears to be no justification for Lewis and Randall's statement that "there is no reason to suppose that solutions (*i.e.*, of $N_2O_4 + NO_2$) in chloroform are non-ideal." In fact there is every reason to expect non-ideal behaviour in chloroform and all these solvents.

The standard free energy of dissociation in the liquid phase $\Delta G^* = -\boldsymbol{R}T \ln K_c'$ is 5330 cal./mole of N_2O_4. This is the change in free energy when *one mole of* N_2O_4 dissociates into *two moles of* NO_2 *at unit concentration.*

The standard entropy of dissociation of N_2O_4 in the liquid phase (ΔS^*) varies from 54·4 cal./(deg. mole) in benzene solution to 43·0 in the pure liquid. The value in the gaseous phase is 35·7.

The enthalpy of dissociation in the liquid (ΔH_l^*) can be found either from the temperature-dependence of K_c' or from the combination of thermal data for the gaseous phase with the heats of solution (L_1^*, L_2°) here determined. The Scheme displays the enthalpy relations, and from it may be read the relation between the enthalpies of dissociation in the liquid and the gaseous phase

$$\Delta H_l = L_2^\circ + \Delta H_g - 2L_1^*$$

Since the heat of solution of NO_2 (L_1^*) can scarcely be negative, a *maximum* value for the enthalpy of dissociation in the liquid is obtained when the heat of solution of NO_2 (L_1^*) is zero; therefore the upper limit for the enthalpy of dissociation in the liquid is 20·880 cal./mole of N_2O_4.

In fact L_1^* is 1560 cal./mole of NO_2. Previously it was thought to be only 700 cal. and the enthalpy of dissociation in the liquid 19,500 cal./mole of N_2O_4. The value of the latter now found, 17,820 cal./mole of N_2O_4, is further from the limit, and the value of L_1^* seems physically more reasonable. In other solvents the enthalpies of dissociation of N_2O_4 ranging from 18,800 cal./mole of N_2O_4 in carbon tetrachloride to 22,200 in benzene have been reported. (Their precision is not high, however, and the heat of dissociation of N_2O_4 in carbon tetrachloride does not differ significantly from its value in the pure liquid.)

APPENDIX

ALLOWANCE FOR GAS IMPERFECTIONS AND THE PRECISION OF GASEOUS EQUILIBRIUM DATA.—1. *Composition of the gaseous phase.* If f_1 and f_2 are the fugacities of NO_2 and N_2O_4 in the equilibrium mixture, then the quotient (f_1^2/f_2) is the equilibrium constant K_f where $K_f = \exp(-\Delta G^\circ/\boldsymbol{R}T)$.

If it is assumed that the fugacities in the gaseous mixture satisfy Lewis and Randall's rule and that the partial pressures of the separate constituents (y_1P and y_2P) satisfy the equations

$$y_1PV = \boldsymbol{R}T(1 + \lambda_1 P) \quad \text{and} \quad y_2PV = \boldsymbol{R}T(1 + \lambda_2 P)$$

then

$$f_1 = y_1P \exp(\lambda_1 P) \quad \text{and} \quad f_2 = y_2P \exp(\lambda_2 P)$$

and

$$K_p = y_1^2P/y_2 \quad = \quad K_f \exp[(2\lambda_1 - \lambda_2)P]$$

A value of $\lambda_1 = -0{\cdot}005$ atm.$^{-1}$ at 21·1°, identical with that for carbon dioxide, was chosen; the Berthelot equation which predicts that $\lambda \propto T^{-3}$ was used to derive λ at other temperatures than the b. p. For N_2O_4 the value of $\lambda_2 = 2\lambda_1$ was chosen originally by Bodenstein and Boës, Verhoek and Daniels, and Giauque and Kemp in order to simplify the calculations. This choice leads to $K_f = K_p$, and permits the evaluation of the mole fractions (y_1 and y_2) from the equations:

$$y_1{}^2P/y_2 \equiv K_p = K_f = \exp(-\Delta G^\circ/\boldsymbol{R}T)$$

Excellent consistency is achieved on this basis, and as the experimental data are not precise enough to justify a different choice, the same value $\lambda_2 = -0{\cdot}01(T/294)^3$ is used here. To obtain the concentrations of NO_2 and N_2O_4 in the gaseous phase (c_1 and c_2) from the mole-fractions of NO_2 and N_2O_4 in the gaseous phase (y_1 and y_2) and the vapour pressure (P) defining equations $c_i = y_iP/\boldsymbol{R}T(1 + \lambda_iP)$ are used ($i = 1, 2$).

2. *Derivation of K_f from P–V–T data.* When Giauque and Kemp applied their corrections to derive a best value of K_f, they had to use P–V–T data. They replaced the simple equation for the dissociation of N_2O_4, *viz.*, $(PV)_{\text{obs.}} = \boldsymbol{R}T(1 + \alpha)$ by $(PV)_{\text{obs.}} = \boldsymbol{R}T(1 + \alpha + \lambda_2P)$. If α' represents the term $(PV)_{\text{obs.}}/\boldsymbol{R}T - 1$, *i.e.*, the uncorrected degree of dissociation evaluated by neglecting gas imperfections, then their treatment leads to:

$$K_F = 4(\alpha' - \lambda_1P)^2P/[1 - (\alpha' - \lambda_2P)^2]$$

(In their paper[3] this equation for K_p appears erroneously with positive signs in the parentheses.)

3. *Consistency of results.* The value of K_f at 21·15°/1 atm. used here is 0·104 atm., which corresponds to a degree of dissociation $\alpha = 0{\cdot}159$. This value is obtained directly from Giauque and Kemp's tables, although in their text[3] they state that $K_f = 0{\cdot}106$ atm., corresponding to a degree of dissociation $\alpha = 0{\cdot}161$ is the best experimental value. The inconsistency is only apparent; combination of their value $\Delta H_0{}^\circ = 12{,}875 \pm 16$ cal./mole of N_2O_4 with that of $\Delta\{(G^\circ - H_0{}^\circ)/T\}$ at 21·15° leads to $\Delta G^\circ = 1325 \pm 16$ cal./mole of N_2O_4, *i.e.*, to $K_f = 0{\cdot}104 \pm 0{\cdot}004$ atm.

4. *Liquid–vapour equilibrium. The Clapeyron–Clausius equation for a dissociating imperfect gas.* To an excellent degree of approximation the exact form of Clapeyron–Clausius equation $\mathrm{d}P/\mathrm{d}T = L/T\,\Delta V$ can here be written:

$$\mathrm{d}P/\mathrm{d}T = L_e/TV_g$$

The equation of state of the gas is here not $PV_g = \boldsymbol{R}T$ but $PV_g = \boldsymbol{R}T(1 + \alpha + \lambda_2P)$ where α is the degree of dissociation, λ_2 the second virial coefficient of the dimer, and $\boldsymbol{R}$ refers to 1 formula weight of dimer, and the approximate form of the Clapeyron–Clausius equation becomes:

$$\boldsymbol{R}T^2(\mathrm{d}\ln P/\mathrm{d}T) = L_e/(1 + \alpha + \lambda_2P)$$

From Giauque and Kemp's interpolation formula the left-hand side is 8020 cal.; $(1 + \alpha + \lambda_2P)$ is 1·149 at the b. p. and hence L_e is 9210 cal./mole of N_2O_4. The calorimetric value is 9110 ± 9. The agreement here is better than that found for acetic acid liquid–vapour equilibrium.

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