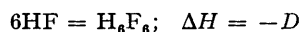


337. Thermodynamic Properties of a Saturated Polymerising Vapour.
Part I. The Liquid-Vapour Equilibrium for Hydrogen Fluoride.

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Theoretical expressions have been derived for the temperature coefficient of the latent heat of vaporisation (dL/dT) and for the curvature of the saturation-vapour pressure line ($d\Lambda/dT$) of hydrogen fluoride. In the saturated vapour, over the temperature range where reliable experimental data are available for comparison, monomer and hexamer are the predominant species. The quantitative predictions of this Part I are made on the basis of the single mobile ideal-gas equilibrium



Predicted and experimentally observed values for dL/dT and for $d\Lambda/dT$ are compared. Discrepancies are greater than those found in similar comparisons for the dimerising species formic acid, acetic acid, and nitrogen dioxide; this is a consequence of the poorer experimental data (especially the absence of thermodynamic equilibrium constants, and data for vapour imperfections) and the over-simplification of the model.

The possibility of making corrections for non-ideal behaviour, and the form of such corrections, are discussed in an Appendix.

THE earliest evidence for extensive association in gaseous hydrogen fluoride appears to be that of Thorpe and Hambly.¹ Much work has appeared since, and convenient summaries may be found in Simons's book² (for work up to 1950) and in the papers of Smith³ and Franck *et al.*⁴ The association gives rise to various anomalies of which the most familiar are those in the volumetric^{4,5} (P - V - T) and spectroscopic³ behaviour, and the most striking are those in the thermal properties.^{4,6} Thus, the specific heat at constant pressure⁴ and the thermal conductivity⁶ are, respectively, 24 and 16 times as great as would be the case in the absence of association. Quantitative interpretations²⁻⁷ of these anomalies (which much exceed those found in dimerising vapours) have been given in terms of mobile equilibria between either a series of oligomers (in which the monomer and hexamer usually predominate), or an infinite series of polymers, or, most simply, in terms of a single, six-fold association (monomer \rightleftharpoons hexamer).

The saturated vapour of hydrogen fluoride is also anomalous. Calorimetric measurements^{8,9} show that between 0° and 20° the latent heat of vaporisation increases with

¹ Thorpe and Hambly, *J.*, 1889, **55**, 189.

² Simons, "Fluorine Chemistry," vol. I, Academic Press, New York, 1950.

³ Smith, *J. Chem. Phys.*, 1958, **28**, 1040.

⁴ Franck, Meyer, and Spalhoff, *Z. Elektrochem.*, 1957, **61**, 348, 993; 1959, **63**, 571, and references therein.

⁵ Briegleb and Strohmeier, *Z. Elektrochem.*, 1953, **57**, 662, 668, and references cited therein.

⁶ Brokaw and Butler, *J. Chem. Phys.*, 1957, **26**, 1636.

⁷ Maclean, Rossotti, and Rossotti, *J. Phys. Chem.*, 1961, **65**, 1376, and references cited therein; *J. Inorg. Nuclear Chem.*, 1963, in the press.

⁸ Fredenhagen, *Z. anorg. Chem.*, 1933, **210**, 210.

⁹ Hu, Johnston, and White, *J. Amer. Chem. Soc.*, 1953, **75**, 5642.

increasing temperature. Recent measurements¹⁰ of saturation vapour pressure show that a graph of $\log P$ versus $1/T$ is concave upwards, *i.e.*, in a direction opposite to normal. [If the saturated-vapour pressure results are represented by an Antoine equation, *i.e.*, as $\log P = a - b/(t_c^\circ + c)$, the constant c is found to be greater than 273° .] No quantitative explanation of this behaviour has been offered, though it has been surmised¹⁰ that its qualitative origin lies in the association.

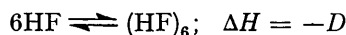
Accordingly, it is our purpose in this paper to determine whether the anomalous behaviour of the saturated vapour can be interpreted quantitatively. No previous quantitative investigations of a saturated polymerising vapour have been made, although numerical predictions¹¹ of the properties of a dimerising vapour have been tested for formic acid, acetic acid, and nitrogen dioxide.

The model adopted in Part I for hydrogen fluoride is a simple equilibrium between monomer and hexamer. Though a dimer and a tetramer have been identified, and play a significant part at low pressures, it seems clear that, in the region of temperature and pressure (along the saturation line) where comparison between theory and experiment can be made, monomer and hexamer are considerably more abundant and important than any other species. This is supported by calculations made from the best available estimates^{3,4} for the association constants K_6 , K_4 , and K_2 , and by the fact that Jarry and Davis¹⁰ could correlate all their density (P - V - T) data along the saturation line on the assumption of a single hexamerisation. Moreover, even outside this region, fairly wide success attends the use of this model in a variety of applications (*e.g.*, heat capacity,⁴ thermal conductivity,⁶ and volumetric behaviour²⁻⁷), and there is to date^{3,5,7} no general agreement on the relative importance of dimer, tetramer, or species higher than hexamer.

The thermodynamic theory for the saturated vapour of an m -fold associating gas has been developed elsewhere. Those results¹² may be adopted with only two alterations. First, it is here more convenient (especially for comparison with Part II) to work in terms of β , the degree of association of monomer, instead of the degree of dissociation of m -mer. Secondly, it is advantageous to present results in terms of the individual latent heats of vaporisation introduced in the numerical discussion¹¹ of saturated dimerising vapours (rather than in terms of heat capacities at constant pressure).

In principle, imperfect-gas behaviour should be taken into account (*e.g.*, by employing equilibrium constants in terms of fugacities). Unfortunately, despite the luxuriance of the literature, such data are not available. An Appendix indicates the lines along which such corrections should be incorporated. In Part II the properties of the sharply contrasting model of an infinite series of polymers are examined.

The Basic Equations.—The chemical equilibrium between hydrogen fluoride monomer and hexamer in the gaseous phase can be written



Let β be the degree of association of the monomer. If a quantity of vapour whose mass is equal to the formula weight of the monomer (*i.e.*, 20.01 g. of hydrogen fluoride) is considered, there are $(1 - \beta)$ moles of monomer and $\beta/6$ mole of hexamer, with a total of $(1 - 5\beta/6)$ mole.

The equation of state. Where the gases are ideal and Dalton's law is obeyed, the equation of state of the mixture (20.01 g. basis) is:

$$PV_g = RT(1 - 5\beta/6), \quad (1)$$

and the partial pressures of the individual constituents are

$$p_6 = P\beta/(6 - 5\beta) = \beta RT/6V_g \quad (2)$$

and

$$p_1 = P(1 - \beta)/(1 - 5\beta/6) = (1 - \beta)RT/V_g. \quad (3)$$

¹⁰ Jarry and Davis, *J. Phys. Chem.*, 1953, **57**, 600.

¹¹ Armitage and Gray, *Trans. Faraday Soc.*, 1962, **58**, 1746.

¹² Gray, *Proc. Roy. Soc.*, 1961, *A*, **264**, 516.

Nomenclature. Different symbols have been used by various authors: generally, experimental results are presented in terms of the temperature, either the pressure or the density, and a parameter related to β . Fredenhagen⁸ used the apparent molecular weight $M = \rho RT/P$, where ρ is the density. Jarry and Davis¹⁰ used $Z = \rho RT/M_1 P$, the association factor, which is also f , the compressibility factor of Briegleb and Strohmeier,⁵ and of Franck *et al.*⁴ M_1 is the molecular weight of monomer, and $M = ZM_1$.

Since the volume of one formula-weight of monomer is $V^g = M_1/\rho$, it can be seen that $(1 - 5\beta/6) = PV^g/RT = 1/Z = M_1/M$.

Inter-relation between reference states: individual latent heats. The latent heat of vaporisation can be expressed in terms of one formula-weight of monomer (20.01 g. of hydrogen fluoride). However, for reasons stated elsewhere,¹¹ the discussion of vapour anomalies is best carried out in terms of the three natural reference states—the equilibrium liquid mixture and the individual pure gaseous monomer and hexamer at unit pressure (unit fugacity, for non-ideal gases).

If the enthalpy of mixing of the two gases is zero, then

$$H^g = (1 - \beta)H_1^g + \beta H_6^g/6$$

The expressions $L_1 = H_1^g - H^l$, and $L_6 = H_6^g - 6H^l$, define the individual latent heats of monomer and hexamer. In terms of L_1 and L_6 , the normal latent heat is given by:

$$L = (1 - \beta)L_1 + \beta L_6/6$$

or

$$L = (1 - \beta)H_1^g + \beta H_6^g/6 - H^l. \quad (5)$$

The enthalpy of de-hexamerisation is given by

$$D = 6H_1^g - H_6^g = 6L_1 - L_6.$$

The Relationship Between L, the Latent Heat of Vaporisation, and Λ , the Apparent Latent Heat.—The apparent latent heat Λ is defined by the equation

$$\Lambda = RT^2 d \ln P/dT \quad (6)$$

and, from the Clapeyron–Clausius equation,

$$L = TP(V^g - V^l) d \ln P/dT.$$

Further, if V^l is neglected as being small by comparison with V^g , and PV^g is substituted from the equation of state, (1) above, then

$$L = RT^2(1 - 5\beta/6) d \ln P/dT.$$

Comparison shows that

$$\Lambda = L/(1 - 5\beta/6). \quad (7)$$

The numerical value of the apparent latent heat of vaporisation. For hydrogen fluoride, Λ can be evaluated both from the saturated-vapour pressure data by eqn. (6), and, if β is known, from the calorimetric latent heats by eqn. (7).

Between 0° and 19.5° (the boiling point) the two sets of values of Λ can be compared. The values of Λ derived from the saturated-vapour pressure equation of Jarry and Davis¹⁰ by eqn. (6) are 5900 cal./mole at 0° and 6050 cal./mole at 19.5°.

Calorimetric measurements give $L = 1704, 1751, \text{ and } 1780$ cal./20.01 g. at 4.40°, 17.56°, and 19.54° (Fredenhagen⁸), and $L = 1789$ cal./20.01 g. at 19.5° (Hu, Johnson, and White⁹): we have adopted 1785 and 1680 cal./20.01 g. at 19.5° and 0°, respectively. For β at 19.5°, the value derived from the Z of Jarry and Davis is 0.897 (this is an extrapolated value); at 0° the value for β according to Fredenhagen is 0.874.

Thus, at 19.5°, we find Λ from calorimetric measurements is 7060 cal. At 0°, Λ is

6200 cal. The agreement at 0° is good; the discrepancy at 19.5° is rather large and may reflect experimental difficulties in the measurement of L as well as errors in β .

The Variation of the Degree of Association with Temperature.—The variation of β with temperature along the saturation line, $(d\beta/dT)_{\text{sat.}}$, is required for the determination of dL/dT and $d\Lambda/dT$ from eqns. (5) and (7).

Both monomer and hexamer obey the Clapeyron–Clausius equation, and since there are $(1 - \beta)$ moles of monomer in the vapour at equilibrium

$$\frac{L_1(1 - \beta)}{P_1 T (V_g - V^l)} = \frac{d}{dT} (\ln p_1).$$

Similarly, for the hexamer

$$\frac{L_6 \beta}{6 P_6 T (V_g - V^l)} = \frac{d}{dT} (\ln p_6).$$

By subtracting the latter equation from the former, replacing P_1 by $P(1 - \beta)/(1 - 5\beta/6)$, and P_6 by $P\beta/(1 - 5\beta/6)$, it follows that

$$\frac{(L_1 - L_6)(1 - 5\beta/6)}{P(V_g - V^l)T} = \left[\frac{d}{dT} \left(\ln \frac{(1 - \beta)}{\beta} \right) \right]_{\text{sat.}},$$

whence

$$\frac{(L_1 - L_6)(1 - 5\beta/6)}{P(V_g - V^l)T} = - \frac{1}{\beta - \beta^2} \left(\frac{d\beta}{dT} \right)_{\text{sat.}}.$$

Then, ignoring the liquid volume, and replacing PV_g by $RT(1 - 5\beta/6)$, we have

$$\left(\frac{d\beta}{dT} \right)_{\text{sat.}} = \frac{(\beta - \beta^2)(L_6 - L_1)}{RT^2}. \quad (8)$$

Since $(\beta - \beta^2)$ is always positive, $(d\beta/dT)_{\text{sat.}}$ is positive when $L_6 > L_1$, negative when $L_6 < L_1$, and zero when $L_6 = L_1$.

The Temperature-dependence of the Latent Heat of Vaporisation.—The latent heat of vaporisation of a liquid normally decreases as the temperature increases, reaching zero at the critical point. Polymerising vapours frequently show anomalous behaviour arising from the mobile equilibrium in the gaseous phase.

Now (5) may be differentiated with respect to temperature along the saturated line:

$$dL/dT = (d/dT)_{\text{sat.}} [(1 - \beta)H_1 + (\beta/6)H_6] - (dH^l/dT)_{\text{sat.}}$$

The last term is equal to

$$\left(\frac{\partial H^l}{\partial T} \right)_p + \left(\frac{\partial H^l}{\partial P} \right)_T \left(\frac{dP}{dT} \right)_{\text{sat.}},$$

which reduces without appreciable error to its first member C_p^l . The term for the gaseous phase, since the mixture is taken to be ideal, is

$$(1 - \beta)C_{p1}^g + (\beta/6)C_{p6}^g + (H_6/6 - H_1)(d\beta/dT)_{\text{sat.}}$$

Now $H_6 - 6H_1 = L_6 - 6L_1$ and therefore, by using eqn. (8) for $(d\beta/dT)_{\text{sat.}}$, it follows that

$$dL/dT = \beta C_{p6}^g/6 + (1 - \beta)C_{p1}^g - C_p^l + (\beta - \beta^2)(6L_1 - L_6)(L_1 - L_6)/6RT^2. \quad (9)$$

This expression can be divided into two parts: the normal or “frozen” contribution $(dL/dT)_f = (\beta C_{p6}^g/6) + (1 - \beta)C_{p1}^g - C_p^l$, and the “reactive” contribution $(dL/dT)_r = (\beta - \beta^2)(6L_1 - L_6)(L_1 - L_6)/6RT^2$. The latter is due to the mobile equilibrium between monomer and hexamer in the gaseous phase.

The "frozen" contribution to dL/dT . This "frozen" contribution to dL/dT corresponds to the relation $dL/dT = C_p^g - C_p^l$ for (ideal) normal non-associating vapours, and is usually negative. The value of the "frozen" thermal capacity of the vapour is not directly determinable, but sufficient spectroscopic data may be available to estimate C_p^g . The value of C_p^g presents more difficulties, which have been discussed elsewhere¹¹ in connection with dimerisation; in the last resort a guess may have to be made.

The heat capacity of the liquid is readily measured, but frequently the measurements have not been taken above 300°K and part of the range of interest is not covered. Extrapolation to higher temperatures may be unsatisfactory.

The "reactive" contribution to dL/dT . This "reactive" contribution is

$$(\beta - \beta^2)(L_1 - L_6)(6L_1 - L_6)/6RT^2.$$

For a given temperature, this contribution is largest when $\beta = 1/2$; it is zero when $\beta = 0$ or $\beta = 1$; it is positive when $L_1 > L_6$, vanishes when $L_1 = L_6$, and is negative when $L_1 < L_6$ (provided that $0 < L_6 < 6L_1$, a condition which is always satisfied where polymerisation occurs under saturated conditions in the vapour).

For a prescribed value of L_1 , the largest negative anomaly occurs where $L_6 = 7L_1/2$; this anomaly vanishes as L_6 approaches $6L_1$.

The numerical values of dL/dT for hydrogen fluoride. Numerical values of dL/dT obtained experimentally are compared in Table 1 with those calculated on the basis of simple hexamerisation in the gaseous phase.

TABLE 1.

Calculated and experimental values of dL/dT for hydrogen fluoride.

Temperature (°C)	-45	0	19.5	50	100
β , the degree of association	0.908	0.874	0.897 *†	0.802 †	0.711 †
L [cal. (20.01 g.) ⁻¹]	1433 *	1683 †	1785 †	2063 †	2780 †
C_p^l (cal. mole ⁻¹ deg. ⁻¹)	10.2	11.5	12.1	13.0	14.5
$(dL/dT)_t$ (cal. mole ⁻¹ deg. ⁻¹)	-3.2	-4.5	-5.1	-6.0	-7.5
$(L_1 - L_6)$ (cal. mole ⁻¹)	2580	242 ₅	1180	299 ₇	240 ₆
$(dL/dT)_r$ [cal. (20.01 g.) ⁻¹ deg. ⁻¹]	13 ₉	11.8	2.7	15.3	11.9
$(dL/dT)_{calc.}$ [cal. (20.01 g.) ⁻¹ deg. ⁻¹]	10.7	7.3	-2.4	9 ₃	4 ₄
$(dL/dT)_{exptl.}$ [cal. (20.01 g.) ⁻¹ deg. ⁻¹]	—	24.0 *†	16.5 ₄ *†	12.3 †	9.3 †
		6.5 †			

* Extrapolated values. † From the data of Jarry and Davis. ‡ Calorimetric values.

The experimental values for dL/dT are of two sorts, as there are calorimetric values^{8,9} of L and values derived¹⁰ by using the exact form of the Clapeyron–Clausius equation.

The values of dL/dT are obtained graphically from these values of L . The calorimetric values of L and dL/dT , whilst internally consistent, disagree with the equally consistent values¹⁰ derived from the saturated-vapour pressure. The values of dL/dT are listed in Table 1.

To calculate dL/dT requires values of C_{p1}^g , C_{p6}^g , C_p^l , β , L_1 , L_6 at any one temperature. Franck's⁴ estimate of $C_{p1}^g = 7$ cal./mole °C, (which implies that $\Delta C_p = 0$ and $C_{p6}^g = 6C_{p1}^g$) seems reasonable. It corresponds to classically excited rotational and translational contributions to the heat capacity but to no vibrational contributions in the monomer, and to 17 fully excited vibrations (out of 30 possible) in the hexamer.

The thermal capacity of the liquid has been measured⁹ up to the boiling point, where it is 12.09 cal./mole °C, and values at higher temperatures are found by extrapolation, whence $(dL/dT)_t$ is found to be approximately -5 cal./mole °C.

Values of β for the saturated vapour may be obtained from the work of Fredenhagen, of Franck *et al.*, and of Jarry and Davis. Fredenhagen⁸ listed apparent molecular weights

of the saturated vapour from -50° to 20° , and Jarry and Davis¹⁰ gave association factors at temperatures up to 105° . These two compilations disagree at the boiling point. For higher temperatures (in the region of appreciable liquid volume) Franck *et al.*⁴ have tabulated densities and pressures for the saturated vapour.

Values of L_1 and L_6 are obtained from values of L , β , and D (eqn. 5). For L , the low-temperature values have already been discussed; values at higher temperatures have been taken from Jarry and Davis.¹⁰ The value of D taken in the present work is 40 kcal./mole. Values for D close to 40 kcal./mole have been determined by many authors, whose results have been summarised by Franck and Meyer;^{4c} a value $D = 39.7$ kcal./mole can also be obtained from the data of Jarry and Davis¹⁰ for the saturated vapour on the assumption of a single hexamerisation.

The calculated and observed values of dL/dT compared in Table 1 agree in sign but do not give good agreement in size. The origin of the discrepancy is unlikely to arise from any error in $D (= 6L_1 - L_6)$, since previous estimates of D are in very good agreement. It reflects errors in the term $(L_1 - L_6) [= D(1 - 5\beta/6) - 5L]$ which, as a small difference between larger quantities, is especially sensitive to errors in L and β . Thus, at 0° the value of β derived from Fredenhagen⁸ gives excellent agreement between observation and calculation, while the value of β derived from Jarry and Davis¹⁰ (which is an extrapolated value) does not. At 50° and 100° agreement between theory and the experimental data of Jarry and Davis¹⁰ is as good as can be expected. Perfect agreement is in any case not to be expected because of the neglect of (a) species other than monomer and hexamer, and (b) deviations from ideal-gas behaviour.

The Curvature of the Vapour Pressure Line.—The slope of the plot of $R \ln P$ against $1/T$ is equal to $-\Lambda$, and so $d\Lambda/dT$ is a good measure of the curvature of the vapour pressure line. For ideal, non-associating gases, $\Lambda = L$, and $d\Lambda/dT$ is equal to dL/dT .

For an ideal hexamerising vapour:

$$\Lambda = L/(1 - 5\beta/6),$$

and differentiation along the saturation line with respect to temperature gives

$$\frac{d\Lambda}{dT} = \left[\frac{dL}{dT} / \left(1 - \frac{5\beta}{6} \right) \right] + \left[\frac{5L}{6} \left(\frac{d\beta}{dT} \right)_{\text{sat.}} / \left(1 - \frac{5\beta}{6} \right)^2 \right].$$

Then, by substitution of

$$dL/dT = C_{pT}^g - C_p^l + \frac{1}{6} (L_6 - 6L_1) d\beta/dT_{\text{sat.}}$$

and $L = (1 - \beta)L_1 + (\beta L_6/6)$; it follows that

$$\frac{d\Lambda}{dT} = \frac{C_{pT}^g - C_p^l}{(1 - 5\beta/6)} - \frac{(L_1 - L_6)}{6(1 - 5\beta/6)^2} \left(\frac{d\beta}{dT} \right)_{\text{sat.}}$$

whence, by putting $(d\beta/dT)_{\text{sat.}} = (\beta - \beta^2)(L_6 - L_1)/RT^2$,

$$\frac{d\Lambda}{dT} = \frac{C_{pT}^g - C_p^l}{(1 - 5\beta/6)} + \frac{(\beta - \beta^2)}{(1 - 5\beta/6)^2} \frac{(L_1 - L_6)^2}{6RT^2}. \quad (10)$$

This expression can be separated into two parts, the "frozen" contribution $(C_{pT}^g - C_p^l)/(1 - 5\beta/6)$, and the "reactive" contribution

$$(\beta - \beta^2)(1 - 5\beta/6)^{-2} (L_1 - L_6)^2/6RT^2.$$

The "frozen" contribution to $d\Lambda/dT$. The "frozen" contribution is negative, and larger than $(dL/dT)_t (= C_{pT}^g - C_p^l)$ since $(1 - 5\beta/6)$ is always less than unity.

The "reactive" contribution to $d\Lambda/dT$. The "reactive" contribution is

$$6(\beta - \beta^2)(L_1 - L_6)^2/[6 - 5\beta]^2RT^2].$$

It is largest where $\beta = 6/7$, (if the variation of L_1 , L_6 , and T^{-2} with temperature is small compared with the variation of β). It can never be negative, since both the term in β , and $(L_1 - L_6)^2$ are positive, but is equal to zero when $L_1 = L_6$ and when $\beta = 1$ or 0.

The numerical value of $d\Lambda/dT$ for hydrogen fluoride. Experimental and calculated values of $d\Lambda/dT$, the curvature of the saturated-vapour pressure line, are compared in Table 2.

TABLE 2.

Calculated and experimental values of $d\Lambda/dT$ for hydrogen fluoride.

Temperature ($^{\circ}\text{C}$)	-45	0	19.5	50	100
$(d\Lambda/dT)_t = (dL/dT)_t/(1-5\beta/6)$	-13.1	-16.6	-20.2	-18.1	-18.4
$(d\Lambda/dT)_t$ (cal. mole $^{-1}$ deg. $^{-1}$)	15.1	9.7	2.0	10.3	4.3
$(d\Lambda/dT)_{\text{calc.}}$ (cal. mole $^{-1}$ deg. $^{-1}$)	2.0	-6.9	-18.2	-7.8	-14.1
$(d\Lambda/dT)_{\text{exptl.}}$ * (cal. mole $^{-1}$ deg. $^{-1}$)	9.8	8.1	7.3	6.3	5.0

* These values are from the first (Antoine) saturated-vapour pressure equation of Jarry and Davis. Their second equation gives only an average value (of 6.4 cal. mole $^{-1}$ deg. $^{-1}$) for $d\Lambda/dT$.

The experimental values of $d\Lambda/dT$ are derived from the saturated-vapour pressure data of Jarry and Davis,¹⁰ who gave two equations for the saturated-vapour pressure

$$\log_{10}(P/\text{mm. Hg}) = 8.38036 - 1952.55/(335.52 + t^{\circ}\text{C})$$

and

$$\log_{10}(P/\text{mm. Hg}) = 1.91173 - 918.24^{\circ}\text{K}/T + 3.21542 \log_{10}(T/^{\circ}\text{K})$$

Both of these equations readily yield¹² values of $d\Lambda/dT$ which are small and positive. Previous saturated-vapour pressure data were adequately represented by a two-constant equation of the form $\log P = a + b/T$ which implied $d\Lambda/dT = 0$.

The data required to calculate $d\Lambda/dT$ have been discussed earlier in this paper, and are found in Table 1. The major point to note is that, since $(L_1 - L_6)$ appears as its square in the expression for $(d\Lambda/dT)_t$, errors in it are very important and failure to use a correct value of β or L will result in considerable error in the calculated reactive contribution to $d\Lambda/dT$. In the case of hydrogen fluoride this error is possibly as much as 40% in the region under consideration.

The agreement between the two sets of values is again poorer than was found for the saturated dimerising vapours of acetic acid, formic acid and nitrogen dioxide, for which corrections for vapour imperfections could be made.

APPENDIX

Allowance for Imperfect-gas Behaviour

In the foregoing account, vapour imperfections have been neglected, partly because the algebra is thus simplified, so that the influence of the mobile equilibrium is more clearly discerned, and partly because the necessary corrections are not precisely known. However, these corrections are not negligible. It is our purpose in this Appendix to indicate how a thermodynamic treatment¹³ for gaseous mixtures in terms of second virial coefficients (*i.e.*, one appropriate to moderate pressures) leads to explicit expressions for the necessary correcting terms.

A 20.01 g. basis (*i.e.*, one formula weight of monomer) is adopted: because some expressions are shorter when written in terms of mole fractions, x is introduced to denote the mole fraction of monomer.

General Expressions in Terms of Second Virial Coefficients, and Some Simplifying

¹³ Guggenheim, "Mixtures," Oxford University Press, 1952.

Assumptions.—The equation of state for a binary mixture of monomeric and hexameric hydrogen fluoride at moderate pressures may be written as:

$$(6 - 5x)PV^g = RT + P[xB_{11} + (1 - x)B_{66} + x(1 - x)(2B_{16} - B_{11} - B_{66})], \quad (\text{A1})$$

where V^g is the volume occupied at pressure P and temperature T by 20.01 g. of hydrogen fluoride, and x is the mole fraction of monomer. B_{11} , B_{66} , and B_{16} are the second virial coefficients corresponding to monomer–monomer, hexamer–hexamer, and monomer–hexamer interactions, respectively. The term $(2B_{16} - B_{11} - B_{66})$ will hereafter be written ΔB for brevity.

In principle, values for B_{11} , B_{66} , and B_{16} for hydrogen fluoride are attainable from experimental measurements; in practice, the available data are not precise enough to permit them to be determined in this way. An empirical estimate of B_{11} might be made by assuming it to be related in some predetermined way to the second virial coefficient of an analogous species such as water, hydrogen chloride, or methyl fluoride. An independent value for B_{66} might be estimated in a similar way but the uncertainties are probably considerable, since $(\text{HF})_6$ has no obvious analogue.

Other associating vapours give rise to similar difficulties. Even in the case of nitrogen dioxide, which is the most precisely investigated associating vapour, Giauque and Kemp¹⁴ did not consider the data good enough to warrant the use of an equation with more than one parameter. Their procedure, which leads to the equation of state

$$PV^g = RT/(6 - 5x) + B_{11}P,$$

is equivalent to the two simplifying assumptions

$$2B_{16} = B_{11} + B_{66} \quad (\Delta B = 0; \text{Lewis and Randall rule}) \quad \text{and} \quad B_{66} = 6B_{11}.$$

Neither assumption has *a priori* justification. The advantage is that, generally speaking, all formulæ are simplified and particular terms (such as γ_1^6/γ_6 or $6H_1 - H_6$) greatly so. Giauque and Kemp¹⁴ employed the further relations

$$B \propto T^{-2} \quad \text{and} \quad dB/dT = -2B/T,$$

which are in accord with the (moderately successful) Berthelot equation, to represent the temperature-dependence of the second virial coefficients.

In this Appendix, formulæ will first be derived in general terms, and the simplifying assumptions made only after the general form has been presented. The following expressions¹³ for chemical potential μ , fugacity coefficient γ , partial molar enthalpy, and partial molar volumes will be required:

$$\mu_1 = \mu_1^\circ + RT \ln(\gamma_1 xP),$$

$$RT \ln \gamma_1 = B_{11}P + (1 - x)^2 \Delta B \cdot P, \quad (\text{A2})$$

$$\bar{H}_1^g = H_1^{\circ g} + P[B_{11} - T dB_{11}/dT] + [(1 - x)/2]P(\Delta B - T d\Delta B/dT), \quad (\text{A3})$$

$$\bar{V}_1^g = RT/P + B_{11} + (1 - x)^2 \Delta B. \quad (\text{A4})$$

Corresponding expressions may be written for μ_6 , γ_6 , \bar{H}_6 , and \bar{V}_6 . It is also convenient to re-define the individual latent heats in such a way as to preserve the simplicity of their relation to L (which is directly measurable) and to D . The defining equations are

$$L_1 = H_1^g - H^l, \quad (\text{A5})$$

$$L_6 = \bar{H}_6^g - 6H^l, \quad (\text{A6})$$

$$D = 6\bar{H}_1^g - \bar{H}_6^g = 6L_1 - L_6, \quad (\text{A7})$$

¹⁴ Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

from which it follows that

$$L = \frac{x}{6-5x} L_1 + \frac{1-x}{6-5x} L_6 = \frac{x\bar{H}_1^g + (1-x)\bar{H}_6^g - (6-5x)H^l}{(6-5x)} \quad (\text{A8})$$

The partial molar enthalpies refer to the saturated equilibrium vapour. The corresponding expression for $\Lambda = LRT/PV^g$ (terms of the order of B^2P^2 being ignored) is obtained from (A1) as:

$$\begin{aligned} \Lambda &= L(6-5x) \left[1 - \frac{B_{11}P}{RT} x - \frac{B_{66}P}{RT} (1-x) - \frac{\Delta BP}{RT} x(1-x) \right] \\ &= [x_1\bar{H}_1^g + (1-x)\bar{H}_6^g - (6-5x)H^l] \left\{ 1 - \frac{P}{RT} [xB_{11} + (1-x)B_{66} + x(1-x)\Delta B] \right\} \quad (\text{A9}) \end{aligned}$$

The Variation of x, the Mole Fraction of Monomer, with Temperature.—In the general case, for equilibrium between the equilibrium liquid and any m -mer in the gaseous phase (mole fraction x_m), $m(d\mu^l/dT)_{\text{sat.}} = (d\mu_m^g/dT)_{\text{sat.}}$, or¹⁵

$$(\bar{V}_m^g - mV^l) \left(\frac{dP}{dT} \right)_{\text{sat.}} = (\bar{S}_m^g - mS^l) - \left(\frac{\partial \mu_m^g}{\partial x_m} \right)_{T,P} \left(\frac{dx_m}{dT} \right)_{\text{sat.}} \quad (\text{A10})$$

This expression on rearrangement gives

$$\begin{aligned} \left[\frac{d}{dT} \log_e (x_m P) \right]_{\text{sat.}} &= \frac{L_m}{P(\bar{V}_m^g - mV^l)T} + \\ &\frac{1}{x_m} \left\{ 1 - \frac{RT}{(\bar{V}_m^g - mV^l)} \left[1 + \left(\frac{\partial \log \gamma_m}{\partial \log x_m} \right)_{T,P} \right] \right\} \left(\frac{dx_m}{dT} \right)_{\text{sat.}}, \quad (\text{A11}) \end{aligned}$$

where γ_m is the fugacity coefficient of the m -mer and $L_m = (S_m^g - S^l)T$.

Explicit expressions for \bar{V}_m^g and $(\partial \log \gamma_m / \partial \log x_m)_{T,P}$ for the cases $m=1$ and $m=6$ are substituted into (A11), and the liquid volume is ignored; $\{d \log [x/(1-x)]/dT\}_{\text{sat.}} = (dx/dT)_{\text{sat.}}/x(1-x)$ is formed as the difference between these two expressions. When terms of the order of $(BP/RT)^2$ are ignored

$$\begin{aligned} \left(\frac{dx}{dT} \right)_{\text{sat.}} &\left\{ \frac{1}{x} \left[1 - \frac{B_{11}P}{RT} - \frac{(1-x^2)P\Delta B}{RT} \right] + \frac{1}{(1-x)} \left[1 - \frac{B_{66}P}{RT} - \frac{x(2-x)P\Delta B}{RT} \right] \right\} \\ &= \frac{L_1 - L_6}{RT^2} + \frac{P}{R^2T^3} \{ L_6 B_{66} - L_1 B_{11} + [L_6 x^2 - L_1(1-x)^2] \Delta B \} \quad (\text{A12}) \end{aligned}$$

This general expression for a saturated hexamerising vapour can be simplified if $\Delta B = 0$, $6B_{11} = B_{66}$, and terms of the order of $(BP/RT)^2$ are ignored, to

$$\left(\frac{dx}{dT} \right)_{\text{sat.}} = \frac{x(1-x)(L_1 - L_6)}{RT^2} + \frac{5x(1-x)[xL_1 + (1-x)L_6]B_{11}P}{R^2T^3} \quad (\text{A13})$$

The correcting term in $(dx/dT)_{\text{sat.}}$ is thus

$$5x(1-x)[xL_1 + (1-x)L_6]B_{11}P/R^2T^3.$$

The Variation of L, the Latent Heat of Vaporisation, with Temperature.—Now

$$L = \frac{x\bar{H}_1^g + (1-x)\bar{H}_6^g}{(6-5x)} - H^l \quad (\text{A8})$$

¹⁵ Denbigh, "Principles of Chemical Equilibrium," Cambridge University Press, 1957

and, by differentiating along the saturation line,

$$\frac{dL}{dT} = \frac{(6H_1^g - H_6^g)}{(6 - 5x)} \left(\frac{dx}{dT} \right)_{\text{sat.}} + \frac{x}{(6 - 5x)} \left(\frac{dH_1^g}{dT} \right)_{\text{sat.}} + \frac{(1-x)}{(6 - 5x)} \left(\frac{dH_6^g}{dT} \right)_{\text{sat.}} - \left(\frac{dH^l}{dT} \right)_{\text{sat.}} \quad (\text{A14})$$

Now, since V^l is negligibly small, $(dH^l/dT)_{\text{sat.}} \sim C_p^l$. Further, for any m -mer,

$$\left(\frac{dH_m^g}{dT} \right)_{\text{sat.}} = \left(\frac{\partial H_m^g}{\partial T} \right)_{x,P} + \left(\frac{\partial H_m^g}{\partial P} \right)_{x,T} \left(\frac{dP}{dT} \right)_{\text{sat.}} + \left(\frac{\partial H_m^g}{\partial x} \right)_{P,T} \left(\frac{dx}{dT} \right)_{\text{sat.}}$$

and, explicitly for the monomer, use of relations (A3) and (A4) leads to

$$\begin{aligned} \left(\frac{dH_1^g}{dT} \right)_{\text{sat.}} &= C_{p1}^{\text{og}} + P \frac{d}{dT} \left[B_{11} - T \frac{dB_{11}}{dT} \right] + \frac{(1-x)}{2} P \frac{d}{dT} \left[\Delta B - T \frac{d\Delta B}{dT} \right] \\ &+ \frac{\Lambda P}{RT^2} \left[B_{11} - T \frac{dB_{11}}{dT} + \frac{(1-x)}{2} \left(\Delta B - T \frac{d\Delta B}{dT} \right) \right] + \left(\frac{\partial H_1^g}{\partial x} \right)_{P,T} \left(\frac{dx}{dT} \right)_{\text{sat.}} \end{aligned} \quad (\text{A15})$$

Since, by the Gibbs–Duhem relation, $x(\partial H_1^g/\partial x)_{T,P} + (1-x)(\partial H_6^g/\partial x)_{T,P} = 0$ the final term in (A15), together with its counterpart for the hexamer, have no effect on (A14). (A15) is simplified (by setting $\Delta B = 0$, $6B_{11} = B_{66}$, and $dB/dT = -2B/T$) to

$$\left(\frac{dH_1^g}{dT} \right)_{\text{sat.}} = C_{p1}^{\text{og}} + \frac{3B_{11}P}{T} \left(\frac{\Lambda}{RT} - 2 \right) + \left(\frac{\partial H_1^g}{\partial x} \right)_{T,P} \left(\frac{dx}{dT} \right)_{\text{sat.}} \quad (\text{A16})$$

and

$$\left(\frac{dH_6^g}{dT} \right)_{\text{sat.}} = C_{p6}^{\text{og}} + \frac{18B_{11}P}{T} \left(\frac{\Lambda}{RT} - 2 \right) + \left(\frac{\partial H_6^g}{\partial x} \right)_{T,P} \left(\frac{dx}{dT} \right)_{\text{sat.}} \quad (\text{A17})$$

These, together with the value for $(dH/dT)_{\text{sat.}}$ expressed in (A13), give

$$\begin{aligned} \frac{dL}{dT} &= \frac{x}{(6 - 5x)} C_{p1}^{\text{og}} + \frac{(1-x)}{(6 - 5x)} C_{p6}^{\text{og}} - C_p^l + \frac{x(1-x)(L_1 - L_6)(6L_1 - L_6)}{(6 - 5x)RT^2} + \\ &\left\{ \frac{5x(1-x)(6L_1 - L_6)\Lambda}{(6 - 5x)^2 R^2 T^2} + 3 \left[\frac{\Lambda}{RT} - 2 \right] \right\} \frac{B_{11}P}{T} \end{aligned} \quad (\text{A18})$$

The correcting term in dL/dT is thus

$$\left\{ \frac{5x(1-x)(6L_1 - L_6)\Lambda}{(6 - 5x)^2 R^2 T^2} + 3 \left[\frac{\Lambda}{RT} - 2 \right] \right\} \frac{B_{11}P}{T}$$

The Variation of Λ , the Apparent Latent Heat of Vaporisation, with Temperature.—When the liquid volume and terms of the order of $(BP/RT)^2$ have been neglected, Λ , the apparent latent heat of vaporisation, is given by eqn. (A9). This equation can be differentiated along the saturation line with respect to temperature, giving

$$\begin{aligned} \frac{d\Lambda}{dT} &= \{H_1^g - H_6^g - 5H^l\} \left(\frac{dx}{dT} \right)_{\text{sat.}} \left\{ 1 - \frac{P}{RT} [xB_{11} + (1-x)B_{66} + x(1-x)\Delta B] \right\} + \left[x \left(\frac{dH_1^g}{dT} \right)_{\text{sat.}} \right. \\ &+ (1-x) \left(\frac{dH_6^g}{dT} \right)_{\text{sat.}} - (6 - 5x) \left(\frac{dH^l}{dT} \right)_{\text{sat.}} \left. \right] \left\{ 1 - \frac{P}{RT} [xB_{11} + (1-x)B_{66} + x(1-x)\Delta B] \right\} \\ &- \left[\frac{d}{dT} \left\{ \frac{P}{RT} [xB_{11} + (1-x)B_{66} + x(1-x)\Delta B] \right\} \right]_{\text{sat.}} \left\{ xH_1^g + (1-x)H_6^g - (6 - 5x)H^l \right\} \end{aligned} \quad (\text{A19})$$

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The profusion of terms in (A19) arises because the simple form for Λ obtained in the ideal case (7) cannot be preserved.

Now, setting $\Delta B = 0$, $6B_{11} = B_{66}$, $dB/dT = 2B/T$ substituting from (A15) and (A16), and ignoring terms of the order of $(BP/RT)^2$ gives

$$\begin{aligned} \frac{d\Lambda}{dT} = & \left\{ xC_{p1}^{\circ g} + (1-x)C_{p6}^{\circ g} - (6-5x)C_p^1 \right\} \left[1 - \frac{B_{11}P}{RT} (6-5x) \right] \\ & + \frac{x(1-x)(L_1 - L_6)^2}{RT^2} \left[1 - \frac{B_{11}P}{RT} (6-5x) \right] + \frac{10x(1-x)(L_1 - L_6)\Lambda B_{11}P}{R^2T^2} \\ & + \frac{6B_{11}P}{T} (6-5x) \left(\frac{\Lambda}{RT} - 1 \right) - \left(\frac{\Lambda}{RT} \right)^2 \frac{B_{11}P}{T} (6-5x). \quad (A20) \end{aligned}$$

The correcting term in $d\Lambda/dT$ is thus

$$\begin{aligned} \frac{B_{11}P}{RT} \left\{ \frac{10x(1-x)(L_1 - L_6)\Lambda}{RT^2} + (6-5x) \left[6R \left(\frac{\Lambda}{RT} - 1 \right) - R \left(\frac{\Lambda}{RT} \right)^2 \right] \right. \\ \left. - xC_{p1}^{\circ g} - (1-x)C_{p6}^{\circ g} + (6-5x)C_p^1 - \frac{x(1-x)(L_1 - L_6)^2}{RT^2} \right\} \end{aligned}$$

Numerical Estimate of the Influence of Non-ideality on the Curvature of the Vapour Pressure Line.—It is desirable to investigate the quantitative effects of imperfections. Although no precise value for B_{11} is available, an estimate may be made from the critical constants of hydrogen fluoride⁴ by the Berthelot equation; this leads to $(B_{11}P/RT) = 0.015$ at 0° and 0.05 at 50° . It must be emphasised that such estimates are very rough, particularly because Berthelot's equation does not deal explicitly with associating vapours.

From the equation of state (A1), the values of the degree of association β become 0.85_6 at 0° and 0.74 at 50° ; the uncorrected values were 0.87_4 and 0.80_2 , respectively. To these values of β correspond values of $(L_1 - L_6)$ of 3025 and 4400 cal. mole⁻¹ at 0° and 50° ; uncorrected values were 2425 and 2400 cal. mole⁻¹. These adjustments in β and in $(L_1 - L_6)$ are the principal effects of allowing for vapour imperfections. This is partly a consequence of the simplifying assumptions ($\Delta B = 0$; $6B_{11} = B_{66}$) made in this treatment. On neglecting, for the moment, additional terms * in (BP/RT) , the roughly corrected, calculated values of $d\Lambda/dT$ in cal. deg.⁻¹ mole⁻¹ at 0° and 50° become -0.2 and $+4.2$ (compared with the uncorrected, calculated values of -6.9 and -7.8). Since the experimental values are $+8.1$ and $+6.3$, the agreement between calculation and observation is much improved.

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* When the additional terms explicitly involving the quotient (BP/RT) are evaluated, the net correction to $d\Lambda/dT$ ($+2.3$ at 0° and -3 at 50°) turns out to be a difference between larger quantities, and thus subject to considerable uncertainty.