39. *The Latent Heat of Vaporization and the Thermochemistry of Ethyl Nitrate.*

By Peter Gray, M. W. T. Pratt, and M. J. Larkin.

In order to correlate the existing thermochemical data for ethyl nitrate, reliable latent-heat data are required. To provide these the vapour pressure of ethyl nitrate has been measured from 0° to 68°. The results obtained, combined with existing low-temperature work, can be represented by the Antoine equation: $\log_{10} p$ (mm.) $= 7{\cdot}145 - 1329/(t° \text{c} + 224{\cdot}0°)$. The latent heat of vaporization (kcal. mole^{-1}) at 25° is 8·7; at the b. p. (87·7°/760 mm.) it is 8·1. The Trouton constant (cal. deg.$^{-1}$ mole^{-1}) is 22. The standard enthalpy of formation (kcal. mole^{-1}) at 25° of liquid ethyl nitrate is $-45{\cdot}7$ and of gaseous ethyl nitrate is $-37{\cdot}0$.

Three experimental determinations have been made from which the enthalpy of formation of ethyl nitrate may be calculated. The first was made in 1876 by Berthelot,[1] who measured directly the heat liberated during the esterification of liquid ethanol with pure nitric acid:

$$\text{EtOH(l)} + \text{HNO}_3\text{(l)} \longrightarrow \text{EtO{\cdot}NO}_2\text{(l)} + \text{H}_2\text{O(l)};\ \Delta H = -\ 6{\cdot}2 \text{ kcal. mole.}^{-1}$$

The second was made in 1886 by Thomsen,[2] who measured the heat of combustion of gaseous ethyl nitrate:

$$\text{EtO{\cdot}NO}_2\text{(g)} + 1{\cdot}75\text{O}_2 \longrightarrow 2\text{CO}_2 + 2{\cdot}5\text{H}_2\text{O(l)} + 0{\cdot}5\text{N}_2;\ \Delta H = -\ 324{\cdot}04 \text{ kcal. mole}^{-1}$$

The most recent was made in 1947 by Wheeler, Whittaker, and Pike[3] who measured the heat of explosion of ethyl nitrate in a closed bomb in the absence of air; the quantity they measured, described as a "calorific value," corresponds to the equation:

$$\text{EtO{\cdot}NO}_2\text{(l)} \longrightarrow 0{\cdot}5\text{N}_2 + (1 + x)\text{CO} + (1 - x)\text{CO}_2 + (2{\cdot}5 - x)\text{H}_2 + x\text{H}_2\text{O(l)};\ \Delta U = -\ 77{\cdot}6 \text{ kcal. mole}^{-1}$$

where x has a value between 0 and 1 which depends on the extent of the water-gas reactions. This possible variation in x affects the derived enthalpy of formation of ethyl nitrate by only 0·1 kcal. mole^{-1}.

Table 1. *Experimental values (kcal. mole^{-1}) for the enthalpy of formation at* 25° *of ethyl nitrate.*

Investigator	Experimental quantity measured	Result (kcal. mole^{-1})	Enthalpy of formation (kcal. mole^{-1}) Liquid	Gas
Berthelot	Esterification of liquid	6·2	−45·6	*−36·9* *
Thomsen	Combustion of vapour	324·04	*−43·6* *	−34·9
Wheeler, Whittaker, and Pike	Explosion of liquid (constant vol.)	77·6	−45·9	*−37·2* *

* Figures in italics are derived from the new latent-heat data.

There are no other primary determinations. For a commentary on the confusion surrounding the various values in standard compilations see the report of Hurwitz and Laidler.[4]

When these experimental results are combined with modern thermochemical data[5] the three values for the enthalpy of formation listed in Table 1 are derived.

Two of these figures apply to the liquid and one to the gas. To correlate them and assess their reliability accurate latent-heat data at 25° are necessary. Although there are

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[1] See Berthelot, "Explosives and their Power," translated by Hake and Macnab, John Murray, London, 1892, p. 279.

[2] Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1886, Vol. IV; *Z. phys. Chem.*, 1905, **52**, 343.

[3] Wheeler, Whittaker, and Pike, *J. Inst. Fuel*, 1947, **20**, 137.

[4] Hurwitz and Laidler, Naval Ordnance Contract 10,260, Report CU/P/54.3.

[5] "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Circular 500, U.S. Dept. of Commerce, Washington, D.C., 1952.

vapour-pressure measurements by Goodeve,[6] at low temperatures (−80° to +20°) these are not accurate enough to give more than a mean latent heat of vaporization at −30°. Accordingly measurements have been made of the vapour pressure of ethyl nitrate from 0° to 68° and the Clausius-Clapeyron equation used to derive a value for the latent heat of vaporization at 25°.

Discussion.—When the Clausius–Clapeyron equation is applied to the vapour-pressure data the enthalpy of vaporization at 25° is found to be 8·7 kcal. mole^{-1}. This value has been used in conjunction with the primary experimental data to compare the values for the enthalpy of formation of gaseous and liquid ethyl nitrate. In Table 1 figures in italics are those obtained by means of the new latent-heat data.

It will be seen that Berthelot's determination agrees very well with that of Wheeler, Whittaker, and Pike: Thomsen's result is (numerically) lower. In the past numerous corrections—of which the most notable is that of Kharasch [7] who altered Thomsen's thermometer readings to the hydrogen scale—have been made to Thomsen's combustion figures. From Thomsen's data Kharasch derives for ΔH_f° $EtNO_3$(l) the value −45·2 kcal. mole^{-1}. Other authorities take other values.

In assessing the merits of the three figures and of their various emended values an important factor is the actual magnitude of the experimental measurement. Thus Berthelot's measurement of 6·2 kcal. mole^{-1}, even if in error by 5%, would lead to an error in heat of formation of only between 0·5 and 1% (0·3 kcal. in 45 kcal.). For Wheeler, Whittaker, and Pike's measurements to achieve the same final accuracy their "calorific value" of 77 kcal. must be correct to 0·5%; this is within the limits of modern calorimetry though the authors estimate conservatively an error of about 1%. At the other extreme is Thomsen's value of 324 for the heat of combustion. This needs to be known to 0·1% to reach the same standard of accuracy and however much Thomsen's data of 1886 are corrected they are unlikely to produce a figure as reliable as the other two.

Accordingly we have adopted the values listed in Table 2 for the standard thermodynamic properties of ethyl nitrate. Entropy and free energy figures are based on the low-temperature calorimetry by Gray and Smith.[8]

TABLE 2. *Principal chemical thermodynamic properties of ethyl nitrate.*

Enthalpy of formation at 25° of liquid	−45·7 kcal. mole^{-1}
,, ,, gas	−37·0 ,,
Latent heat (ΔH_v) of vaporization at 25°	8·7 ,,
,, ,, ,, b. p.	8·1 ,,
Entropy (relative to absolute zero) at 25° of liquid	59·08 cal. deg.$^{-1}$ mole^{-1}
Entropy of formation at 25° of liquid	−118·1 ,, ,,
Gibbs free energy of formation (ΔF_f°) at 25° of liquid	−10·5 kcal. mole^{-1}

EXPERIMENTAL

Materials.—Pure ethyl nitrate supplied by the Explosives Research and Development Establishment, Waltham Abbey, was dried ($CaCl_2$) and fractionally distilled.

Apparatus and Method.—Standard apparatus was used for measuring vapour pressures. A bulb containing the sample of ethyl nitrate was connected to a mercury manometer. The liquid was frozen and the air was removed. The bulb and manometer were immersed in a water-bath. The height of the mercury was measured by a cathetometer. Allowance was made for the variation in density of the mercury.

TABLE 3. *Vapour pressure of ethyl nitrate. Interpolated values of vapour pressure from* 0° *to* 60°.

Temp. (c)	0·0°	10·0°	20·0°	30·0°	40·0°	50·0°	60·0°
Vapour pressure (mm. Hg)	16·3	29·2	49·9	81·8	129	197	292

Results.—*Vapour pressure.* Over a hundred readings of vapour pressure and temperature were taken between 20° and 68°. Readings were also made between 0° and 20° to overlap with Goodeve's data.[6] Table 3 gives some interpolated values at 10° intervals. The results obtained

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[6] J. W. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 501.

[7] Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359.

[8] Gray and Smith, *J.*, 1954, 769.

in the range 0—20° coincide with those of Goodeve, who derives the expression $\log_{10} p$ (mm.) = 8·57 − 2010/T° K and thus the effective temperature range extends down to −80°. Additional points above the range of vapour-pressure measurement made here are provided by b. p. data. At 728·4 mm. the b. p.[9] is 86·3°. At 760 mm. the b. p. is 87·7° (Timmermans and Mattaar[10] give 88·7° ± 0·1°; Perkin[11] gives 87·5—87·7°; Lecat[12] gives 87·68°). When all these results are represented as a graph of log p against 1/T° K a curved line results, indicating departure from the approximate relation $\log p = A + B/T$. All the data are fitted by the Antoine equation $\log_{10} p$ (mm. Hg) = 7·035 − 1278/(t° C + 219·3°) (which has three empircal constants instead of two).

Latent Heat of Vaporization. The Clausius–Clapeyron equation, $\mathrm{d}p/\mathrm{d}T = \Delta H_v/T\Delta V$, may be used in its approximate form $\mathrm{d}\ln p/\mathrm{d}T = \Delta H_v/\boldsymbol{R}T^2$ to derive the latent heat of vaporization from the vapour-pressure equation, if the vapour is assumed to behave as a perfect gas. The uncertainty introduced by this assumption is probably less than 0·1 kcal. mole^{-1}. At 25°, ΔH_v = 8·7 kcal. mole^{-1}. At the normal b. p., ΔH_v = 8·1 kcal. mole^{-1}. The temperature variation of the latent heat may be conveniently represented over the temperature range −80° to +80° by the approximate expression ΔH_v (kcal. mole^{-1}) = 8·9$_5$ − t° C/100. Application to this expression of Kirchoff's equation, $\mathrm{d}\Delta H_v/\mathrm{d}T = C_p$ (gas) − C_p (liquid), yields C_p (gas) − C_p (liquid) = −10 cal. deg.$^{-1}$ mole^{-1}. The specific heat of the liquid has been measured,[8] and at 25° is 40·7 cal. deg.$^{-1}$ mole^{-1}. Thus at this temperature C_p (gas) is approximately 31 cal. deg.$^{-1}$ mole^{-1}. Of this quantity 23 cal. deg.$^{-1}$ mole^{-1} arise from internal motions (vibrations and internal rotations). The ethyl nitrate molecule contains eleven atoms and is not linear, so that if all the possible vibrations are active they will contribute $(3 \times 11 - 6)\boldsymbol{R}$ = 53·6 cal. deg.$^{-1}$ mole^{-1} to the specific heat. Therefore the temperature variation of the latent heat of vaporization suggests that at room temperature about one half of the possible vibrations of gaseous ethyl nitrate are active.

Entropy of vaporization. From these figures the standard entropy of vaporization (cal. deg.$^{-1}$ mole^{-1}) at the b. p. (Trouton's constant) is 22. This is much more satisfactory than that of 26 calculated by Goodeve from her low-temperature results.

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DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF CAMBRIDGE.

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[9] Kopp, *Annalen*, 1856, **98**, 367.
[10] Timmermans and Mattaar, *Bull. Soc. chim. belges*, 1921, **30**, 218.
[11] Perkin, *J.*, 1889, **55**, 680.
[12] Lecat, *Ann. Soc. sci. Bruxelles*, 1927, I, **47**, 153.