414. *The Latent Heats of Vaporization of the Alkyl Nitrates.*

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The vapour pressures of *n*- and *iso*-propyl and *n*- and *iso*-butyl nitrate have been measured from 0° to 70°, and their normal b. p.s have been remeasured. From these results accurate values are derived for the latent heats of vaporization of the nitrates at 25° and at their boiling points by means of the Clausius–Clapeyron equation. Corrections for gas imperfection and finite liquid volume are applied to this equation, and previously existing latent-heat determinations for methyl and ethyl nitrate are also corrected. The following values (kcal. mole^{-1}) for ΔH_v at 25° have been found for the alkyl nitrates: Me 8·15; Et 8·67; Pr^n 9·70; Pr^i 9·27; Bu^n 10·42; Bu^i 10·08. Latent heats at the b. p. are also recorded; all the Trouton "constants" (cal. deg.$^{-1}$ mole^{-1}) are about 22·5 ± 0·5. The variation with temperature of latent heat indicates that at room temperature fewer than half the possible vibrational modes are active in the gaseous nitrates.

THE latent heats of vaporization of only three alkyl nitrates have been measured.[1] McKinley-McKee and Moelwyn-Hughes [2] measured the vapour pressure of methyl nitrate over a range of temperature and deduced the latent heat of vaporization as 7·728 kcal. mole^{-1} at 64·6°, the normal boiling point. They did not correct their results for gas imperfections and this value needs revision. The vapour pressure of ethyl nitrate has been measured at moderate,[3] low,[4] and high [5] temperatures and its latent heat of vaporization found [3] to be ~8·7 kcal. mole^{-1} at 25°. An empirical equation for the vapour pressure of *iso*propyl nitrate is also available.[6]

The importance of such latent heat information was shown in a previous paper [3] in which a new measurement of the latent heat of vaporization of ethyl nitrate was used to deduce the best values for the standard enthalpies of formation of liquid and gaseous ethyl nitrate. The results chosen on this basis as the best available—enthalpy of formation at 25° of liquid ethyl nitrate, −45·7 kcal. mole^{-1}, and of gaseous ethyl nitrate, −37·0 kcal. mole^{-1}—have now been substantiated by Skinner and Fairbrother,[7] who from the heat of combustion, showed that the enthalpy of formation of liquid ethyl nitrate is −45·51 ± 0·25 kcal. mole^{-1}.

We have now measured the vapour pressures of *n*- and *iso*-propyl and *n*- and *iso*-butyl nitrate over the range 0—70°, and have remeasured their normal boiling points, as the literature values are discordant. Empirical equations relating vapour pressure and

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[1] Gray and Pratt, XXVIII Congr. Ind. Chem., Madrid, 1955.
[2] McKinley-McKee and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247.
[3] Gray, Pratt, and Larkin, *J.*, 1956, 210.
[4] Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 501.
[5] Hildenbrand and Whittaker, *J. Phys. Chem.*, 1955, **59**, 1024.
[6] Technical Data Sheet, Ethyl Corp., Detroit.
[7] Skinner and Fairbrother, personal communication.

temperature (Antoine equations) which are also satisfied by the normal boiling points have been fitted to the experimental results. The latent heats of vaporization of the four nitrates at 25° and at their boiling points have been derived from the Antoine equations by means of the Clausius–Clapeyron equation; corrections have been applied for non-ideal gas behaviour and for finite liquid volume.

In what follows we use the symbolism in the annexed Table.

a, A, b, B, D, X, Y	Arbitrary constants
C_p (cal. deg.$^{-1}$ mole^{-1})	Molar specific heat at constant pressure
δ	Fractional error involved in using approx. form of the Clausius–Clapeyron eqn.
M	Mol. wt.
n	No. of atoms in a molecule
p (mm. Hg)	Saturation v. p. at t° c
ρ_l (g. cm.$^{-3}$)	Density of liquid at t° c
t (° c), T (° K)	Temperature
T_b (° K)	B. p.
T_c (° K)	Critical temp.
V_c (cm.^{3} mole^{-1})	Critical volume
V_g (cm.^{3} mole^{-1})	Volume of 1 mole of gas at T° and p mm. pressure
V_l (cm.^{3} mole^{-1})	Volume of 1 mole of liquid at T° and p mm. pressure

Empirical Vapour-pressure Equations.—Plots of $\log_{10} p$ against $1/T$ are shown in the Figure for the propyl and butyl nitrates, with, for comparison, the vapour-pressure curves of methyl [2] and ethyl nitrate.[3] The curves depart only very slightly from straight lines in the range 0—70° c. B. p. data for the higher nitrates show that curvature increases at higher temperature. This non-linearity indicates departure from the approximate relation $\log p = A + B/T$, and the vapour pressure results are fitted to the Antoine equation $\log_{10} p = A - B/(t + D)$ which has three empirical constants instead of two. The constants of the Antoine equations which best fit all the available vapour-pressure and normal boiling-point data are listed in Table 1, and in Table 2 the experimentally measured vapour pressures are compared with those calculated from the appropriate empirical

Temperature dependence of vapour pressures of six alkyl nitrates.

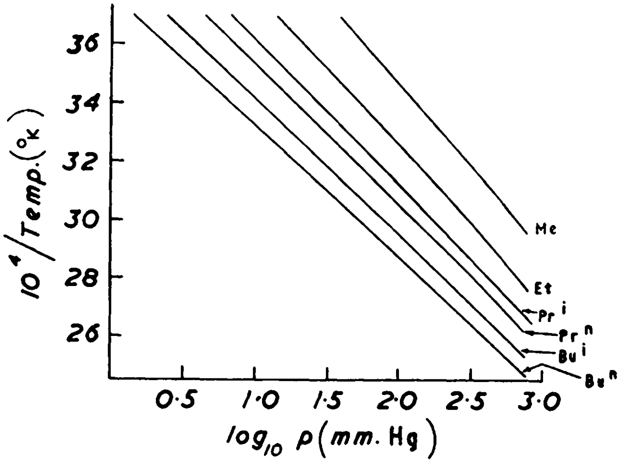

TABLE 1. *Vapour-pressure equations,* $\log_{10} p$ *(mm.* Hg) $= A - B/(t + D)$.*

Nitrate	A	B	D	Nitrate	A	B	D
Ethyl	7·145	1329	224·0°	*n*-Butyl	7·607	1742	235·6°
n-Propyl	7·246	1444	220·8	*iso*Butyl	7·424	1597	228·6
*iso*Propyl	7·303	1457	227·5				

* For methyl nitrate the alternative equation :

$\log_{10} p$ (mm. Hg) $= 26{\cdot}6767 - 6{\cdot}3431 \log_{10} T - 2620{\cdot}1139/T$ has been fitted successfully [3] to the experimental data.

equation. The vapour pressure curve of normal propyl nitrate is close to that found by the Ethyl Corporation,[6] who give the relation $\log_{10} p = 7{\cdot}3506 - 1520/(t + 230)$.

TABLE 2. *Experimental vapour pressures ($p_{\text{exp.}}$, mm.* Hg), *compared with calculated vapour pressures ($p_{\text{calc.}}$) derived from the relations given in Table* 1.

	Ethyl		*n*-Propyl		*iso*Propyl		*n*-Butyl		*iso*Butyl	
Temp. (° c)	$p_{\text{exp.}}$	$p_{\text{calc.}}$	$p_{\text{exp.}}$	$p_{\text{calc.}}$	$p_{\text{exp.}}$	$p_{\text{calc.}}$	$p_{\text{exp.}}$	$p_{\text{calc.}}$	$p_{\text{exp.}}$	$p_{\text{calc.}}$
0	16·1	16·3	5·3	5·1	7·3	7·9	1·7	1·7	2·9	2·7
10	29·4	29·2	10·0	9·8	14·6	14·7	3·3	3·3	5·4	5·4
20	49·5	49·9	17·8	17·7	26·5	26·1	6·3	6·2	10·0	10·0
30	81·5	81·8	30·6	30·8	44·5	44·2	11·1	11·2	17·8	17·7
40	128	129	50·7	51·2	72·1	71·8	18·9	19·3	30·1	30·1
50	198	197	81·4	81·8	113	113	32·1	32·1	48·5	49·0
60	293	292	128	127	172	172	51·8	51·8	77·9	77·8
70	420	422	189	190	256	255	81·1	80·7	120	119
B. p.	760	760	760	760	760	760	760	760	760	760

Latent Heats of Vaporization.—The Clausius–Clapeyron equation is used to derive latent heats of vaporization from the vapour-pressure equations .

$$\Delta H_v = T(V_g - V_l)(\mathrm{d}p/\mathrm{d}T)_{\text{sat.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

An approximate form of this is :

$$(\mathrm{d} \ln p/\mathrm{d}T)_{\text{sat.}} = \Delta H_v/\boldsymbol{R}T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The fractional error δ involved in using eqn. (2) instead of the exact form (1) is estimated as follows. From eqn. (1) :

$$\Delta H_v/\boldsymbol{R}T^2(\mathrm{d} \ln p/\mathrm{d}T) = p(V_g - V_l)/\boldsymbol{R}T = 1 - \delta$$

The assumptions in eqn. (2) are that $V_l = 0$, and that $pV_g = \boldsymbol{R}T$. The fractional error δ is therefore made up of a contribution due to the finite volume of the liquid, δ_l, and a contribution due to gas imperfection, δ_g, *i.e.*, $\delta = \delta_g + \delta_l$.

Correction for Finite Liquid Volume.—δ_l is the fractional error in replacing $p(V_g - V_l)/\boldsymbol{R}T$ by $pV_g/\boldsymbol{R}T$.

Therefore $\qquad \delta_l = pV_l/\boldsymbol{R}T \simeq V_l/V_g$

Now $\qquad V_l = M/\rho_l$

Therefore $\qquad \delta_l = \dfrac{M}{\rho_1} \cdot \dfrac{p}{760} \cdot \dfrac{273}{T} \cdot \dfrac{1}{22{,}400}$

Correction for Gas Imperfection.—δ_g is the fractional error due to assuming $pV_g = \boldsymbol{R}T$, *i.e.*, $\delta_g = 1 - (pV_g/\boldsymbol{R}T)$. We may derive an expression for δ_g, in terms of the critical constants V_c and T_c, from the Berthelot equation :

$$(p + a/TV_g^2)(V_g - b) = \boldsymbol{R}T$$

$$pV_g/\boldsymbol{R}T = 1 + b/V_g - a/\boldsymbol{R}T^2V_g$$

Therefore $\qquad \delta_g = (a/\boldsymbol{R}T^2 - b)/V_g$

Setting $a/\boldsymbol{R}T^2 = 3V_cT_c^2/2T^2$, and $b = V_c/4$, the values adopted[8] by D. Berthelot and found satisfactory for organic vapours by Lambert *et al.*,[9] we have :

$$\delta_g = \frac{V_c}{V_g}\left(\frac{3T_c^2}{2T^2} - \frac{1}{4}\right)$$

Alkyl nitrates are all dangerously explosive and since, as far as we are aware, their critical temperatures and critical volumes have never been measured the approximations

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[8] Partington, " An Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 650.

[9] Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc.*, 1949, *A*, **196**, 113.

$T_c \simeq 1{\cdot}5T_b$ (Guldberg's rule) and $V_c \simeq 3V_l$ (Partington [8]) have been used. To this degree of accuracy:

$$\delta_g = \frac{V_l}{V_g}\left(\frac{81}{8} \cdot \frac{T_b^2}{T^2} - \frac{3}{4}\right)$$

In this equation, V_g may be replaced by its ideal value, $V_g = 22{,}400(T/273)(760/p)$. The approximations involved in the derivations of δ_l and δ_g introduce only minor errors into the latent heats themselves.

In previous work [2-4] the Clausius–Clapeyron eqn. (2) has been used without corrections for the assumptions involved. The opportunity is now taken of correcting the former values of the latent heats of vaporization of methyl and ethyl nitrates at their boiling points.

TABLE 3. *Latent heats and entropies of vaporization of the alkyl nitrates.*

	25°C					Boiling point					
Nitrate	$RT^2 \frac{d \ln p}{dT}$ (cal. mole^{-1})	$10^3\delta_l$	$10^3\delta_g$	$10^3\delta$	Corr. ΔH_v (cal. mole^{-1})	$RT^2 \frac{d \ln p}{dT}$ (cal. mole^{-1})	$10^3\delta_l$	$10^3\delta_g$	$10^3\delta$	Corr. ΔH_v (cal. mole^{-1})	Entropy of vapn. (cal. deg.$^{-1}$ mole^{-1})
Methyl ...	8230	0·5	8·0	8·5	8150	7730	2·4	22·6	25·0	7540	22·3
Ethyl ...	8720	0·3	4·4	4·7	8670	8150	2·9	25·8	28·7	7920	21·9
n-Propyl	9720	0·1	2·3	2·4	9700	8870	3·3	31·0	34·3	8580	22·3
*iso*Propyl	9300	0·2	3·1	3·3	9270	8640	3·4	31·8	35·2	8350	22·2
n-Butyl ...	10,430	0·0	0·9	0·9	10,420	9680	3·6	33·7	37·3	9340	23·1
*iso*Butyl	10,100	0·1	1·5	1·6	10,080	9280	3·8	36·2	40·0	8920	22·7

In Table 3 the corrected and the uncorrected latent heats of vaporization of the six alkyl nitrates are listed, for 25° C and the normal boiling points. The latent-heat values derived here at 25° are the more precise for two reasons. First, the experimental points in this region are more numerous and more precise than near the boiling point. Secondly, at 25° the correction δ is in all cases less than 1·0%; it is least for the least volatile nitrates. At the boiling point the correction is 2—5% and is least for the most volatile nitrates. For this reason when the Clausius–Clapeyron equation is used in its simplified form (2) to derive latent heats at the boiling point there is usually no justification in quoting ΔH_v to more than two significant figures. Very precise equation of state data are needed to obtain values of ΔH_v accurate to ± 5 cal. mole^{-1}. An interesting instance where these complete data are available is provided by nitromethane.[10]

Entropies of Vaporization.—The standard entropies of vaporization at the boiling points (Trouton's " constants ") (see Table 3) lie in the range $22{\cdot}5 \pm 0{\cdot}6$ cal. deg.$^{-1}$ mole^{-1}, indicating that the liquid nitrates are not associated. As the Trouton's " constant " increases only slightly as the series is ascended, the latent heat of higher nitrates may be safely estimated by assuming a Trouton's " constant " of about 23 cal. deg.$^{-1}$ mole^{-1}.

Variation in Latent Heat with Temperature and the Specific Heats in Liquid and Vapour Phases.—Our results for the variation with temperature of the latent heat of vaporization fit, to a first approximation, the equation $\Delta H_v = X - Y(t - 25)$, the calculated values of X and Y being shown in Table 4. Application of the equation $d\Delta H_v/dT \simeq C_p(\text{gas}) - C_p(\text{liquid})$ yields * the values for $C_p(\text{gas}) - C_p(\text{liquid})$ in Table 4. The specific heats of liquid methyl [11] and ethyl nitrates [13] have been measured at 25°. For the other nitrates C_p(liquid) has been estimated by multiplying the molecular weight by the factor

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* The exact form of this equation is:

$$d\Delta H_v/dT = \Delta C_p + L/T - L(d \ln \Delta V/dT)_p$$

For the transition liquid ⟶ gas the second and the third term of this expression are very nearly equal.

[10] McCullough, Scott, Pennington, Hossenlopp, and Waddington, *J. Amer. Chem. Soc.*, 1954, **76**, 4791, and references cited therein.

[11] Gray and Smith, *J.*, 1953, 2380.

0·44. (Experimentally the factor is 0·49 for methyl nitrate, and 0·45 for ethyl nitrate.) Hence C_p(gas) may be estimated.

TABLE 4. *Implications of temperature-dependence of latent heat of vaporization,* ΔH_v (*cal. mole*$^{-1}$) $= X - Y(t - 25)$,* *where* X = *latent heat of vaporization* (*cal. mole*$^{-1}$) *at* 25°, *and* $Y \bumpeq$ *specific heat decrement* (*cal. deg.*$^{-1}$ *mole*$^{-1}$) *on vaporization.* (*Entries, except in the last column, are in cal. deg.*$^{-1}$ *mole*$^{-1}$.)

Nitrate	Y	C_p(liq)	C_p(gas)	C_p(gas) due to internal vibrations (approx.)	C_p(gas) if all $(3n - 6)$ vibrations active (approx.)	Fraction of vibrations active at *ca.* 25° c (approx.)
Methyl	15·7	37·6	22	14	36	0·39
Ethyl	10·3	40·7	30	22	54	0·40
n-Propyl	13·2	46	33	25	72	0·35
*iso*Propyl	11·9	46	34	26	72	0·36
n-Butyl	9·8	52	42	34	90	0·38
*iso*Butyl	11·8	52	40	32	90	0·36

* For ethyl nitrate, valid from − 30° to 110°; for other nitrates from 25° to the normal b. p.

Fraction of Vibrations Active.—The value of the specific heat of the vapour derived above may be used to estimate the fraction of the possible vibrational modes of the nitrates which are active at room temperature.

The contribution to the specific heat of the gas made by the internal motions of the molecule (vibrations, and internal rotations) is C_p(gas) $- 4\boldsymbol{R}$: the term $4\boldsymbol{R}$ is made up of $3\boldsymbol{R}/2$ for translation, $3\boldsymbol{R}/2$ for rotation of the molecule as a whole, and $\boldsymbol{R}$ to convert the specific heat from constant-pressure into constant-volume conditions.

The nitrate molecules are non-linear, so that if all possible vibrations were active, they would contribute $(3n - 6)\boldsymbol{R}$ cal. deg.$^{-1}$ mole^{-1} to the specific heat. Table 4 shows that the contribution made to the specific heat by the internal rotations varies from 35 to 40% of the maximum possible, so that fewer than half the vibrations of the gaseous alkyl nitrates are active at room temperature and the fraction of active vibrations decreases slowly as the series is ascended.

EXPERIMENTAL

Materials.—*n*- and *iso*-Propyl and *n*- and *iso*-butyl nitrate were prepared by fractionating the corresponding alcohols, and adding 35 ml. very slowly from a tap funnel to an ice-cooled mixture of 50 ml. each of concentrated sulphuric and nitric acid. The mixture was vigorously stirred, and the temperature kept below 3°. The ester was decanted, washed immediately with sodium carbonate solution and water, dried ($CaCl_2$), and fractionated under reduced pressure. Physical constants of the purified nitrates are shown in Table 5.

TABLE 5.

Nitrate	B. p./760 mm.	d^{20}	n_D^{20}	Nitrate	B. p./760 mm.	d^{20}	n_D^{20}
Methyl	64·6°	1·205	1·3748	*iso*Propyl	102°	1·05	1·3913
Ethyl	87·7	1·12	1·3857	*n*-Butyl	133	1·03	1·4069
n-Propyl	110	1·06	1·3980	*iso*Butyl	123	1·02	1·4026

The b. p. of *n*-propyl nitrate, which is much higher than the figure (100·5°) quoted by the International Critical Tables,[12] is in agreement with that deduced from the vapour-pressure data of the Ethyl Corporation,[6] and the b. p. given by Wheeler, Whittaker, and Pike.[14] The b. p. of *n*-butyl nitrate, 133°, is 3° lower than that in International Critical Tables; [12] those of *iso*propyl and *iso*butyl nitrate are identical with recorded values.[13]

Apparatus and Method.—The vapour pressures were measured over the range 0—70° at approximately 5° intervals in standard apparatus in which a bulb containing the liquid nitrate was connected to a wide-bore (12 mm.) mercury manometer. The apparatus was immersed in

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[12] Internat. Crit. Tables, McGraw-Hill Book Co., New York, 1927.

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

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

a thermostat. The height of the mercury was measured by a cathetometer, and allowance made for the variation in density of the mercury with temperature. Several samples of each nitrate were used and, to check the purity of the liquid nitrate, the vapour pressure of the last drop left in the apparatus was compared with that of the original volume at the same temperature. The identity of these pressures showed that no fractionation had occurred; the composition of the last drop was the same as that of the bulk.

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