Low-temperature Calorimetry and the Thermodynamic Properties of Ethyl Nitrate.

By Peter Gray and P. L. Smith.

The molar heat capacity C_p of ethyl nitrate has been measured from 20° to 293° K. The m. p. is 178·6° K. On fusion, C_p increases from 27·3 to 38·7 cal. deg.$^{-1}$ mole^{-1}; at 298° K C_p is 40·7. The enthalpy and entropy differences between absolute zero and 298° K (standard state) are 9240 cal. mole^{-1} and 59·08 cal. deg.$^{-1}$ mole^{-1}, respectively.

Existing values of the heat of formation of ethyl nitrate are discussed and a critical selection made of $\Delta H_f{}^\circ = -45\cdot8 \pm 0\cdot8$ kcal. mole^{-1} (liquid). The standard entropy of formation is $-118\cdot1$ cal. deg.$^{-1}$ mole^{-1} and the standard free energy of formation $-\Delta F_f{}^\circ$ is $-10\cdot61$ kcal. mole^{-1}.

The equilibrium constant $K = [C_2H_5 \cdot NO_3][H_2O]/[C_2H_5 \cdot OH][HNO_3]$ of esterification by pure reactants is $4\cdot8 \times 10^4$ and the heat liberated $-\Delta H_{est}$ is 6·4 kcal. mole^{-1}. In aqueous solution heat is absorbed ($\Delta H'_{est} = 3\cdot1$ kcal. mole^{-1}), the free-energy balance is unfavourable, and the equilibrium constant K' is $5\cdot8 \times 10^{-2}$. Similar differences were found for methyl nitrate by Gray and Smith (*J.*, 1953, 2380).

Owing to the explosive character of organic nitrates and the complexity of their decomposition (Gray and Yoffe, *Proc. Roy. Soc.*, 1949, *A*, **200**, 114), the thermodynamic properties of many of them have not been measured, and recorded values of their heats of formation are often discordant.

For the simplest members of the series, methyl and ethyl nitrates, values are available for their heat of formation. To enable free energies of formation, entropies of formation, and equilibrium constants of reactions in which these esters take part to be determined, further data are necessary. These have recently been provided for methyl nitrate by Gray and Smith (*J.*, 1953, 2380). In order to supply similar information for ethyl nitrate, direct measurements have been made of its specific heat from temperatures near the absolute zero to room temperature. The corresponding entropy and enthalpy differences have been evaluated from these and from the latent heat of fusion. The results have been used in calcuations of the heat of formation at absolute zero, the heat of formation of gaseous atoms, the standard free energy of formation, and in applications of these to equilibria. The properties of methyl and ethyl nitrate are compared.

Experimental.

Materials.—Pure ethyl nitrate, supplied by the Explosives Research & Development Establishment, Waltham Abbey, was dried ($CaCl_2$) and fractionally distilled; the middle fraction had b. p. 89°/760 mm.

Apparatus and Method.—For work below 120° K, these are substantially identical with those described by Gray and Smith (*loc. cit.*). However, because of the large heat capacity, to improve thermal couplings between the thermometers and the sample, measurements of thermal capacities above 120° K were made by winding the heating coil and thermometers directly on to the copper can containing the ethyl nitrate. Correction for the heat capacity of the can and the copper shavings present to ensure rapid distribution of heat was computed from published data on copper (*e.g.*, Giauque and Meads, *J. Amer. Chem. Soc.*, 1941, **63**, 1897).

Results.—*Melting point.* Ethyl nitrate melted sharply at 178·6° K (cf. $MeNO_3$, 190·2° K). The value recorded in tables ($-102°$ c) is 7·5° low.

Latent heat and entropy of fusion. The enthalpy of fusion L_f at 178° K was determined from measurements of the amount of heat required to convert solid a little below the m. p. into liquid a little above it. Corrections were made for heat capacities and radiation losses.

$$\text{Molar latent heat of fusion } L_f = 2038 \pm 42 \text{ cal.}$$
$$\text{Molar entropy of fusion} \quad S_f = 11\cdot41 \pm 0\cdot21 \text{ cal. deg.}^{-1}$$

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Heat capacity. Table 1 gives the experimental values of the molar heat capacities C_p in cal. deg.$^{-1}$ measured from 20° to 293° K. From its value at very low temperatures C_p increases continuously up to 27·3 cal. deg.$^{-1}$ mole^{-1} at T_f. No other transitions are observed. Above the m. p., C_p for the liquid increases slowly from 38·7 at T_f to 40·7 cal. deg.$^{-1}$ mole^{-1} at 298° K.

TABLE 1. *Molar heat capacity* C_p *of ethyl nitrate. (Measured values.)*

Temp. (K)	C_p *	Temp. (K)	C_p	Temp. (K)	C_p	Temp. (K)	C_p	Temp. (K)	C_p	Temp. (K)	C_p
	Series I : 0·3316 mole.					Series II : 0·3103 mole.					
21·6°	3·80	51·6°	10·30	91·3°	15·9	128°	19·1	178·6° †	—	220°	39·0
22·3	4·25	62·7	12·12	92·1	15·6	134	19·1	182	38·9	223	39·0
26·1	4·98	67·3	13·00	93·8	16·2	146	20·3	188	38·8	244	40·0
29·2	5·75	77·7	13·60	105·9	16·2	151	20·9	191	39·1	249	39·8
39·0	8·30	81·5	14·4	107·2	16·5	159	21·2	198	39·1	260	40·3
42·5	8·42	84·7	14·6	121	17·9	167	21·8	200	40·0	270	40·4
44·7	9·11	87·1	14·8	124	18·4	169	22·7	208	39·7	280	40·8
48·3	9·50			125	18·0	175	23·4	209	40·0	293	40·0

* C_p is in cal. deg.$^{-1}$ mole^{-1} throughout. † M. p.

These values of C_p are plotted against T. From the smoothed graph obtained (see Figure) values of C_p and of C_p/T were derived. These values are listed in Table 2 and are used in calculations of thermodynamic functions.

TABLE 2. *Molar heat capacity of ethyl nitrate. Interpolated values of* C_p *and* C_p/T *and derived thermodynamic functions (see Figure).*

Temp. (K)	C_p *	C_p/T †	Enthalpy diff.,‡ $H(T)-H(0)$	"Absolute entropy," * $S(T)-S(0)$	Temp. (K)	C_p *	C_p/T †	Enthalpy diff.,‡ $H(T)-H(0)$	"Absolute entropy," * $S(T)-S(0)$
Solid ethyl nitrate					160°	21·50	0·134	2030	24·83
15°	1·50	0·100	5·60	0·50	170	22·45	0·132	—	—
20	3·32	0·166	18·8	1·17	178·6 §	23·3	0·130	2445	. 27·27
25	4·85	0·194	—	—					
30	6·10	0·203	—	—	*Liquid ethyl nitrate*				
35	7·24	0·207	—	—	178·6	38·75	0·217	4485	38·68
40	8·14	0·203	138	5·12	180	38·8	0·216	—	—
45	9·00	0·200	—	—	190	39·1	0·205	—	—
50	9·96	0·199	—	—	200	39·2	0·196	5320	43·11
60	11·72	0·195	337	9·10	210	39·4	0·188	—	—
70	13·10	0·187	—	—	220	39·6	0·180	6110	46·87
80	14·25	0·178	598	12·83	230	39·75	0·173	—	—
90	15·29	0·170	—	—	240	39·9	0·166	6904	50·33
100	16·17	0·162	903	16·13	250	40·05	0·160	—	—
110	17·00	0·154	—	—	260	40·2	0·155	7705	53·54
120	17·95	0·149	1245	19·21	270	40·4	0·150	—	—
130	18·93	0·146	—	—	280	40·5	0·145	8510	56·54
140	19·68	0·141	1620	22·06	290	40·6	0·140	—	—
150	20·72	0·138	—	—	291	40·6	0·140	8960	58·11
					298	40·7	0·137	9240	59·08

* In cal. deg.$^{-1}$ mole^{-1}. † In cal. deg.$^{-2}$ mole^{-1}. ‡ In cal. mole^{-1}.
§ M. p. : $L_f = 2038$ cal. mole^{-1}; $S_f = 11·41$ cal. deg.$^{-1}$ mole^{-1}.

TABLE 3. *Calculation of molar enthalpy (cal. mole^{-1}) of ethyl nitrate relative to absolute zero.*

Debye's T^3 law, 0—15° K	5·60
Graphical integration, 15—178·6° K	2442
Fusion at 178·6° K	2038
Graphical integration, 178·6—298° K	4756
Total $H(298)–H(0)$	9242

TABLE 4. *Calculation of the molar entropy (cal. deg.$^{-1}$) of ethyl nitrate relative to absolute zero (" absolute entropy ").*

Debye's T^3 law, 0—15° K	0·50
Graphical integration, 15—178·6° K	26·77
Fusion, 2038/178·6	11·41
Graphical integration, 178·6—298° K	20·40
Total $S_{abs.}°$ (298)	59·08

Difference between molar heat content at room temperature and at absolute zero. Calculation of the enthalpy difference between 0° and 298·1° K (shown in Table 3) is made partly from numerical integration on the assumption that Debye's T^3 law holds below 15° K, and the remainder from the latent-heat term and a graphical integration of the curve between the C_p curve and the T axis. The difference in molar enthalpy between 0° and 298·1° K is 9240 cal.

Entropy from calorimetric data. Table 4 summarizes an entropy calculation, which is made partly from Debye's T^3 law, partly from graphical integration above and below the m. p., and from the measured entropy of fusion.

Molar heat capacity of ethyl nitrate 15° K to 300° K.
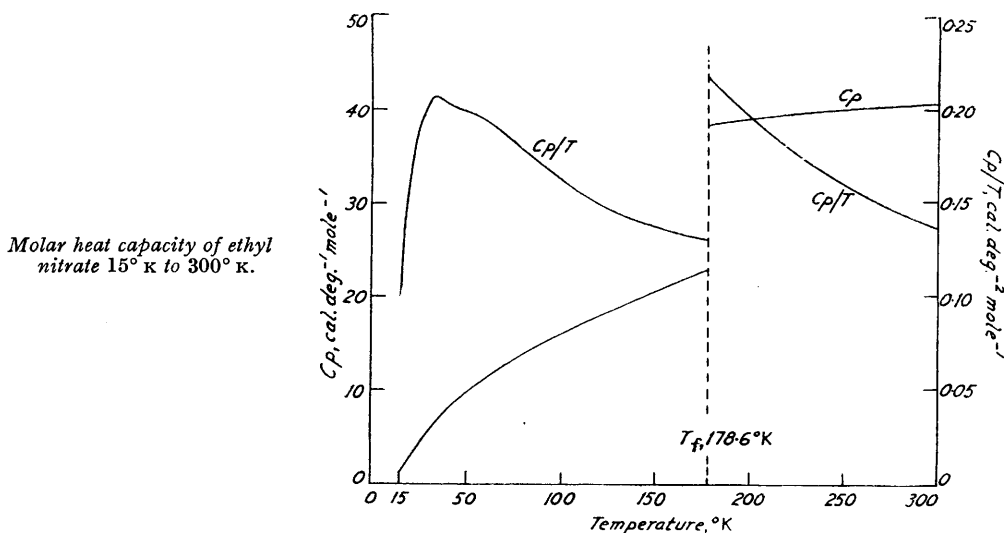
DISCUSSION

These properties of ethyl nitrate may be compared with those recently reported for methyl nitrate by Gray and Smith. They enable values to be derived of the enthalpy, entropy, and free energy of formation under different conditions and to be applied to the reactions of ethyl nitrate.

Physical Properties of Ethyl Nitrate.—Ethyl nitrate melts at 178·6° K ($T_f = -94·6°$ c). The first determination of T_f was made by von Schneider (*Z. physikal. Chem.*, 1897, **22**, 233), who measured temperatures on an iron–constantan thermocouple and found $T_f = -112°$ c. The corrected value given by Timmermans (I.C.T., McGraw Hill, New York, 1927, Vol. I, 306) is $-102°$ c. Errors in these early determinations may be due to glass formation and supercooling. The increase of specific heat at the m. p. from 27·3 for the solid to 38·7 (cal. deg.$^{-1}$ mole^{-1}) for the liquid indicates that other modes of motion as well as translation have come into play. The observed latent heat and entropy of fusion, 2040 cal. mole^{-1} and 11·41 cal. deg.$^{-1}$ mole^{-1}, are typical of compounds free from both phase transitions and specific heat anomalies below the m. p. ; similar behaviour is observed in methyl nitrate.

Thermochemical Properties of Ethyl Nitrate.—(1) *Enthalpy of formation.* Various determinations have been made of the heat of formation of ethyl nitrate. They entail combustion with excess of oxygen, explosion alone, or esterification. The heat of combustion is about 300, of explosion about 80, and of esterification about 5 kcal. mole^{-1}; clearly, although small percentage errors may considerably affect the accuracy of values derived from combustion, explosion is less subject to this, and esterification least of all. All determinations depend, of course, on accurate analyses of reaction products and it is probably analysis errors which limit the accuracy of modern combustion data on such nitrogen compounds. Table 5 lists the values of heat of formation obtained. Some of these refer to the liquid, some to the vapour. The only published value of the heat of vaporization of the liquid available is due to Goodeve (*loc. cit.*) and is based on measurements between $-80°$ c and $+20°$ c. This gives $L_v = 9·2$ kcal. mole^{-1} at 25° c and this value has been used

to correlate the different determinations. It is noteworthy that Berthelot's early determination yields a value closely in agreement with the latest British and American figures, though it is Thomsen's determination which is quoted in standard compilations (*e.g.*,

TABLE 5. *Enthalpy of formation of ethyl nitrate.**

Reference	Thermodynamical quantity determined	Derived enthalpy of formation :	
		liquid	gas
Goodeve [1]	Latent heat of vaporization = 9·2	—	—
Berthelot [2]	Enthalpy of esterification = − 6·2	−46·4	−37·2
Thomsen [3]	Enthalpy of combustion of vapour = − 326·4	−41·7	−32·5
Kharasch [4]	Correction of Thomsen's combustion data = − 322·4 (theoretical work)	−45·7	−36·5
Whittaker, Wheeler, and Pike [5]	Enthalpy of explosion of liquid = − 77·6	−45·7	−36·5
This paper	Adopted value	−45·8	−36·6

* Values are in kcal. mole^{-1} at 298° K. Indirect values (derived from Goodeve's values of L_v = 9·2) are in italics.
[1] *Trans. Faraday Soc.*, 1932, **30**, 501. [2] *Ann. Chim. Phys.*, 1880, **20**, 255. [3] " Thermochemische Untersuchungen," Barth, Leipzig (1882—1886). [4] Personal communication (1945). [5] *J. Inst. Fuel*, 1947, **20**, 137.

Bichowsky and Rossini, " Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, 1936; Nat. Bur. Standards Circular No. 500, " Chemical Thermodynamical Properties," 1950).

The values adopted are (in kcal. mole^{-1}) :

Standard enthalpy of formation of liquid ethyl nitrate $\Delta H_f°(298) = -45\cdot8 \pm 0\cdot8$.
Enthalpy of formation of gaseous ethyl nitrate $\Delta H_f(298) = -36\cdot6 \pm 0\cdot8$.

Berthelot (*loc. cit.*) measured the enthalpy of solution of ethyl nitrate in 180 parts of water as −0·99 kcal. mole^{-1}. Hence the heat of formation of aqueous ethyl nitrate is −46·8 kcal. mole^{-1}. At room temperature, hydrolysis of the ethyl nitrate is much too slow to influence this value.

The value of the standard enthalpy of formation can be combined with the values of the enthalpies of ethyl nitrate and its constituent elements relative to absolute zero determined above to give the value of the molar heat of formation at absolute zero $\Delta H_f(0)$ of ethyl nitrate. The values of $H(298) - H(0)$ kcal. mole^{-1} are : for $C_2H_5\cdot NO_3$, 9·240; for $2C_{graphite}$, 0·503; for $2\cdot5H_2$, 5·084; for $1\cdot5O_2$, 3·105; for $0\cdot5N_2$, 1·036; total for elements, 9·73.

Hence $\Delta H_f(0)(C_2H_5\cdot NO_3) = -45\cdot8 - 9\cdot24 + 9\cdot73 = -45\cdot3 \pm 0\cdot8$ kcal. mole^{-1}.

(2) *Entropy of formation of ethyl nitrate.* The *standard molar entropy of formation* $\Delta S_f°$ may be derived at once from the values of the entropy relative to absolute zero (" absolute entropies ") of liquid ethyl nitrate and of its constituent elements in their standard states. The National Bureau of Standards Circular No. 500 lists values of $S_{abs.}°$ in cal. deg.$^{-1}$ mole^{-1} as $2C_{graphite}$, 2·72; $2\cdot5H_2$, 78·03; $0\cdot5N_2$, 22·88; $1\cdot5O_2$, 73·50; total 177·13; and from this work $S_{abs.}°(EtNO_3) = 59\cdot08$. Hence

$$\Delta S_f° = 59\cdot08 - 177\cdot13 = -118\cdot1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

For ethyl nitrate *vapour* at 298° K under its own vapour pressure of 67·5 mm. Hg

$$S_{abs.}(EtNO_{3,\,g}) = S_{abs.}° + L_v/T = 59\cdot08 + 9200/298 = 89\cdot95 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

For ethyl nitrate *vapour in the (hypothetical) standard state of* 1 atm. pressure at 298° K

$$S_{abs.}°(EtNO_{3,\,g}) = 89\cdot95 + R \ln(67\cdot5/760) = 85\cdot14 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The corresponding *entropy of formation*, $\Delta S_f°(EtNO_{3,\,g})$ is −92·68 cal. deg.$^{-1}$ mole^{-1}.

(3) *Free energy of formation of ethyl nitrate.* The values determined for the entropy of formation can be combined with the heat of formation adopted to calculate the free energy of formation of ethyl nitrate. For the *standard state*—liquid nitrate, 298° K, 1 atm.—since $\Delta H_f° = -45\cdot8$ kcal. mole^{-1} and $\Delta S_f° = -118\cdot1$ cal. deg.$^{-1}$ mole^{-1} we have :

$$\Delta F_f°(C_2H_5\cdot NO_{3,\,l}) = -10\cdot6 \pm 0\cdot8 \text{ kcal. mole}^{-1}.$$

The uncertainty is largely due to the uncertainty in the published values of the heat of formation.

For *gaseous* ethyl nitrate *in the (hypothetical) standard state at* 298° K and 1 atm., the standard molar free energy of formation is similarly obtained. Since $\Delta H_f°(\text{gas}) = -36.6$ kcal. mole^{-1} and $\Delta S_f°(\text{gas}) = -92.68$ cal. deg.$^{-1}$ mole^{-1} we have : $\Delta F_f°(\text{C}_2\text{H}_5\cdot\text{NO}_{3,\,g}) = -9.0$ kcal. mole^{-1}.
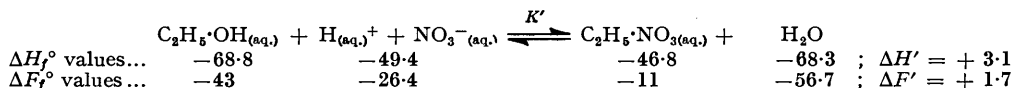
The Reaction between Ethyl Alcohol and Nitric Acid.—Ethyl nitrate is prepared by esterification of ethyl alcohol, and it is desirable to know the thermodynamic functions for this reaction. Values may now be derived for the free-energy changes and hence for the equilibrium constant of the reversible reaction between pure components and of the corresponding reaction in aqueous solution.

(1) *Pure liquids.* Inserting the values derived above, and others tabulated, into the equation for esterification, we have, in kcal. mole^{-1}

	$\text{C}_2\text{H}_5\cdot\text{OH}$	+	HNO_3	$\xrightleftharpoons{K}$	$\text{C}_2\text{H}_5\cdot\text{NO}_3$	+	H_2O		
$\Delta H_f°$ values	-66.36		-41.40		-45.8		-68.32	;	$\Delta H° = -6.36$
$\Delta F_f°$ values	-41.77		-19.10		-10.61		-56.69	;	$\Delta F° = -6.43$
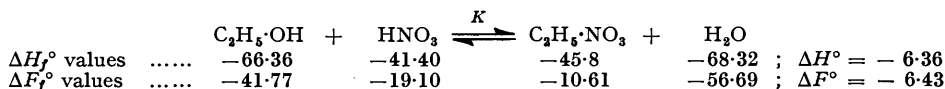
The free-energy change $\Delta F°$ of -6.4 ± 0.8 kcal. mole^{-1} corresponds to a thermodynamic equilibrium constant K where $\log_e K = -\Delta F°/\boldsymbol{R}T$, *i.e.*, $K = 5.1 \times 10^4$. Thus, with pure reactants at room temperature esterification is greatly favoured, and it is this fact which enabled Berthelot to use this reaction to measure the heat of formation of ethyl nitrate; it proceeds virtually to completion, as he found by precipitating and weighing the ester formed.

(2) *Aqueous solutions.* From the heat of formation of aqueous ethyl nitrate and other tabulated values the thermodynamic properties of the esterification in dilute aqueous solution can be evaluated. Nitric acid in dilute solution is effectively completely ionized.

	$\text{C}_2\text{H}_5\cdot\text{OH}_{(aq.)}$	+	$\text{H}_{(aq.)}^+$	+ $\text{NO}_3{}^-_{(aq.)}$	$\xrightleftharpoons{K'}$	$\text{C}_2\text{H}_5\cdot\text{NO}_{3(aq.)}$	+	H_2O		
$\Delta H_f°$ values...	-68.8		-49.4			-46.8		-68.3	;	$\Delta H' = +3.1$
$\Delta F_f°$ values...	-43		-26.4			-11		-56.7	;	$\Delta F' = +1.7$

Esterification is now endothermic ($\Delta H = 3.1$ kcal. mole^{-1}) and hydrolysis is favoured in aqueous solutions not only by mass-action effects but by the alteration in the thermodynamic equilibrium constant to $K' = 0.058$, almost 10^6 times smaller than its value for pure reactants. Thermodynamics, as usual, tells us nothing about the rates at which these equilibria are attained. Experimentally, it is known that the hydrolysis of ethyl nitrate at room temperature is quite slow and Berthelot's value for its heat of solution is not in error from this source.