

485. *The Thermodynamic Properties of Methyl Nitrate.*

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The heat capacity C_p of methyl nitrate has been measured from 13° to 295° K. The melting point T_f is 190.2° K. No other transitions or phase changes were observed. The molar latent heat of fusion L_f is 1.970 kcal. and the molar entropy of fusion S_f is 10.36 e.u. The absolute molar entropy of the liquid at 1 atm. and 298° K, $S_{\text{abs.}}^{298}$, is 51.86 e.u. and the standard molar entropy of formation ΔS_f is -92.72 e.u. The enthalpy (heat content) difference between 298° K and absolute zero is 8.256 kcal. mole⁻¹. The specific heat at 298° K of liquid methyl nitrate is 37.57 cal. mole⁻¹ deg.⁻¹ or 0.483 cal. g.⁻¹ deg.⁻¹.

The values of the thermodynamic functions just derived have been applied to some reactions of methyl nitrate to give values of enthalpy and free energy balances and equilibrium constants in some of its important reactions. Thus, the best value for the standard heat of formation of liquid methyl nitrate ΔH_f^{298} being taken as -37.2 ± 0.8 kcal. mole⁻¹, the standard free energy of formation ΔF_f^{298} is -9.55 ± 0.8 kcal. mole⁻¹, both values referring to 25° C and 1 atm.

The equilibrium constant $[\text{ester}][\text{water}]/[\text{acid}][\text{alcohol}]$ of the reaction between pure nitric acid and methyl alcohol by which it is normally prepared is $K = 2.3 \times 10^5$ and the heat liberated $-\Delta H_{\text{est.}}$ is 7.08 kcal. mole⁻¹; and from kinetic measurements on the reverse reaction the velocity constant of esterification should be $k_2 = 4 \times 10^{-6}$ l. mole⁻¹ sec.⁻¹ at room temperature. All these values are in agreement with Berthelot's work on ethyl nitrate where esterification was found to be rapid and complete and $\Delta H_{\text{est.}}$ was -6.2 kcal. mole⁻¹.

METHYL NITRATE is the simplest of the nitrate esters and its investigation has thrown light not only on its own properties but also on those of its homologues. Because of its explosive character little experimental work on it has been published; its melting point is here recorded for the first time and until the recent war no experimental value was available for its heat of formation.

In order to supply such information direct measurements have been made of the specific heat of pure methyl nitrate from temperatures near the absolute zero to room temperature,

and the corresponding entropy and enthalpy differences have been evaluated from this and from the latent heat of fusion. These results have been used in calculations of the heat of formation at absolute zero, the heat of formation from gaseous atoms, and the standard free energy of formation, and in applications of these to equilibria.

EXPERIMENTAL

Materials.—Pure methyl nitrate was supplied by the Explosives Research and Development Establishment (Waltham Abbey). It was dried over calcium chloride and fractionally distilled at atmospheric pressure. It boiled at 64.6°. The initial and final fractions were rejected. This material had n_D^{20} 1.3760₅.

Apparatus.—A thin-walled copper calorimeter containing two resistance thermometers (constantan for temperatures below 22° K and platinum for higher temperatures) was suspended in a conventional cryostat. An outer vacuum-jacket in direct contact with the refrigerant enclosed a helium liquefier of the Simon expansion type, which, however, was not used in this work. Temperatures below 20° K were obtained by controlled pumping in liquid hydrogen. A copper radiation shield was attached to the expansion chamber, and a high vacuum was maintained during measurements.

Automatic temperature control operated between 20° and 60° K and above 90° K, and the rapid-pumping system enabled measurements to be made nearly to room temperatures. These refinements are the essential differences between this apparatus and that described by Parkinson, Simon, and Spedding (*Proc. Roy. Soc.*, 1951, *A*, **207**, 137).

Method.—Methyl nitrate was sealed in a small copper can under 1 atm. pressure of helium. This atmosphere, and a few copper shavings in the can, ensured rapid distribution of heat without undue increase in thermal capacity. Correction for the heat capacity of the copper container and shavings was computed from published data on copper (*e.g.*, Giauque and Meads, *J. Amer. Chem. Soc.*, 1941, **63**, 1897).

Specific heat values were taken under non-adiabatic conditions, *i.e.*, the calorimeter was always slightly above or below the temperature of its surroundings, and the corresponding small linear drifts were observed before and after heating. These drifts were extrapolated to the mid-point of the heating period to yield the exact temperature rise.

The latent heat was obtained by setting the temperature of the calorimeter a few degrees below the m. p. of methyl nitrate and taking one or two heat capacity points, thus increasing the temperature nearly to the m. p. A continuous current was then passed through the heater and a temperature-time plot made. The melting period could clearly be seen, and immediately on the completion of melting further heat capacity points were taken. The total heat supplied for melting could then be computed.

RESULTS

Melting Point.—Methyl nitrate melted quite sharply at 190.2° K (cf. HNO₃, 231° K; EtNO₃, 161° K).

Heat of Fusion.—The heat of fusion at 190.2° K was determined as described (see above), and gave:

$$\begin{aligned} \text{latent heat of fusion } L_f &= 1970 \text{ cal./mole} \\ \text{entropy of fusion } S_r &= 10.36 \text{ e.u./mole} \end{aligned}$$

These values, in agreement with Walden's empirical rule (1908; quoted by, *e.g.*, Glasstone, "Textbook of Physical Chemistry," MacMillan, 3rd Edn.) $L_f \doteq 13.5T$, are typical of compounds from which transitions below the m. p. and specific heat anomalies are absent (Ubbelohde, *Quart. Reviews*, 1950, **4**, 356). On melting, new modes of motion as well as translation come into play, as the increase of 8 cal. in the molal heat capacity (from 22.7 to 30.6 cal.) shows.

Heat Capacity.—Table 1 and the Figure give the absolute heat capacities C_p of methyl nitrate in cal. deg.⁻¹ mole⁻¹ measured from 14° to 291° K. The specific heat of solid methyl nitrate increases regularly from its low value at 14° K to its value at the m. p. without any discontinuity. Melting is accompanied by an increase of specific heat and the specific heat of the liquid continues to rise up to 295°, the last temperature at which measurements were made, to the value $c_p = 0.483 \text{ cal. g.}^{-1} \text{ deg.}^{-1}$ ($C_p = 37.5 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$). From a plot C_p-T smoothed values of the heat capacity were obtained by interpolation, and the derived quantity C/T was calculated from them. These values are listed in Table 2 and are used in calculations of the thermodynamic functions.

TABLE 1. *Molar heat capacity, C_p , of methyl nitrate.*

Temp. (κ)	Molar specific heat (cal. mole ⁻¹ deg. ⁻¹)	Temp. (κ)	Molar specific heat (cal. mole ⁻¹ deg. ⁻¹)	Temp. (κ)	Molar specific heat (cal. mole ⁻¹ deg. ⁻¹)	Temp. (κ)	Molar specific heat (cal. mole ⁻¹ deg. ⁻¹)
<i>Series I.</i> 0-1085 mole.		<i>Series I.</i> 0-1085 mole.		<i>Series II.</i> 0-268 mole.		<i>Series II.</i> 0-2680 mole.	
13·95°	0·985	44·6°	7·45	93·0°	14·3	216·5	33·5
14·45	1·05	45·3	8·30	95	14·3		
15·07	1·18	46·1	8·30			230	35·0
15·77	1·34			100·6	15·0		
16·6	1·53	52·9	8·94	102·7	14·8	244	35·9
17·94	1·85	54·1	9·40	104·9	15·1		
19·11	2·22					265·3	36·8
		62·7	10·2	121·5	16·6		
20·16	2·35	64·6	10·4	123·5	16·6	277	37·5
21·57	2·62	66·4	10·6				
22·92	2·86			138	18·4	295·5	37·3
24·60	3·25						
26·16	3·72			151·2	19·1	<i>Series III.</i> 0-2534 mole.	
28·22	4·25			152·9	19·5	193·7°	31·17
33·05	5·03			174·5	21·4	200	32·17
34·35	5·83			179·5	22·8	204·4	32·60
35·3	6·96					207	32·92
36·4	6·91			181·0	23·0		
37·45	6·82						
38·3	6·82			190·2 = Melting point.			

TABLE 2. *Heat capacity, C_p , of methyl nitrate. Interpolated values of C_p and C_p/T taken from smoothed plot of C_p-T (see Figure).*

Temp. (κ)	Specific heat (cal. mole ⁻¹ deg. ⁻¹)	C_p/T	Enthalpy difference (cal. mole ⁻¹)	Entropy difference (cal. mole ⁻¹ deg. ⁻¹)	Temp. (κ)	Specific heat (cal. mole ⁻¹ deg. ⁻¹)	C_p/T	Enthalpy difference (cal. mole ⁻¹)	Entropy difference (cal. mole ⁻¹ deg. ⁻¹)
(T)	(C_p^{solid})		$H(T)-H(0)$	$S(T)-S(0)$	(T)	(C_p^{liquid})		$H(T)-H(0)$	$S(T)-S(0)$
<i>Solid.</i>					<i>Liquid.</i>				
20°	2·40	0·110	13·35	0·840	190·2°	Fusion	—	$L_f = 1970$	$S_f = 10,360$
25	3·30	0·132	—	—	190·2	30·60	0·160	4483	35,960
30	4·55	0·152	—	—					
35	6·05	0·173	—	—	200	32·05	0·160	4759	37,370
40	7·30	0·183	107·05	3,924	210	33·17	0·158	—	—
45	8·20	0·182	—	—	220	34·07	0·155	5422	40,530
50	8·95	0·179	—	—	230	34·90	0·152	—	—
60	10·25	0·171	282	7,498	240	35·60	0·148	6120	43,560
70	11·55	0·165	—	—	250	36·15	0·145	—	—
80	12·65	0·158	509	10,774	260	36·60	0·141	6842	46,450
90	13·75	0·153	—	—	270	36·96	0·137	—	—
100	14·75	0·147	785	13,816	280	37·25	0·133	7581	49,270
110	15·67	0·143	—	—	290	37·45	0·129	—	—
120	16·52	0·138	1100	16,656					
130	17·50	0·135	—	—	291·2	37·48	0·1285	7992	50,710
140	18·40	0·131	1453	19,348	298·2	37·57	0·126	8256	51,860
150	19·35	0·129	—	—					
160	20·25	0·127	1841	21,912					
170	21·10	0·124	—	—					
180	21·90	0·122	2263	24,376					
190	22·65	0·119	—	—					
190·2	22·70	0·119	2513	25,596					

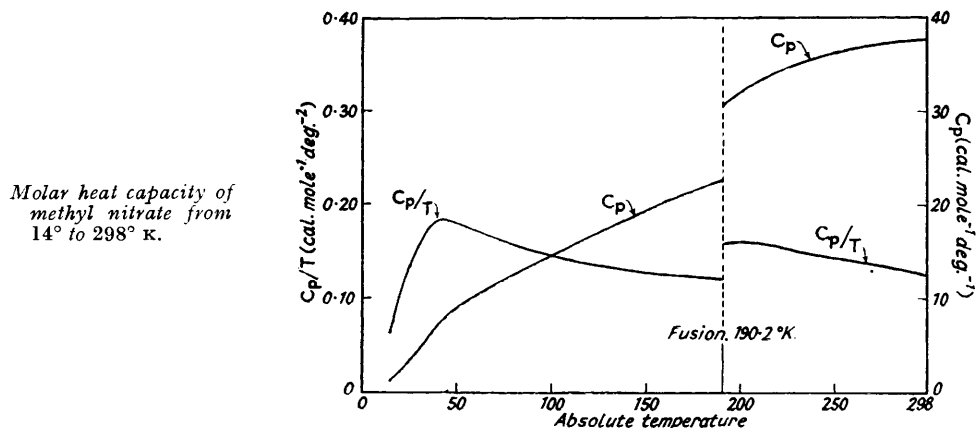
Difference between Heat Content at Absolute Zero and Room Temperature.—Calculation of the enthalpy difference between 0° and 298·1° κ is shown in Table 3.

TABLE 3. *Calculation of the molar enthalpy of methyl nitrate relative to absolute zero.*

	Cal. deg. ⁻¹
Debye's T^3 law, 0—13·95° κ.....	3·46
Graphical integration, 13·95—190·2° κ	2510
Fusion at 190·2° κ	1970
Graphical integration, 190·2—298·1° κ	3773
Total $H^{298}-H^0$	8256

The calculation is made partly from numerical integration on the assumption that Debye's T^3 law holds below 14°K , and the remainder from the latent-heat term and a graphical integration of the area between the C_p curve and the T axis. The difference in enthalpy between 0° and 298.1°K is $8156 \text{ cal. mole}^{-1}$.

Entropy from Calorimetric Data.—Table 4 illustrates an entropy calculation, which is made partly from the Debye T^3 law below 14°K , the remainder from the latent-heat term and an



integration of the area between the plot of C_p/T and the T axis. The "absolute entropy" per mole of liquid methyl nitrate at 25°C is $S_{\text{abs.}}^{298} = 51.86 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$.

TABLE 4. Calculation of the entropy of methyl nitrate relative to absolute zero ("absolute entropy").

Debye's T^3 law, $0-13.95^\circ \text{K}$	e.u. 0.328
Graphical integration, $13.95-190.2^\circ \text{K}$	25.268
Fusion, $1970/191.2$	10.36
Graphical integration, $191.2-298.1^\circ \text{K}$	15.90 ₄
Total ($S^{298.1}$)	51.86

The entropy of formation in the standard state from its elements is thus :

$$\Delta S_f^{298} = S_{\text{CH}_3\text{NO}_3}^{298} - \Sigma S_{\text{elements}} = 51.86 - 144.58^* \\ \Delta S_f^{298} = -92.72 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

DISCUSSION

The values of the thermodynamic functions just derived may be applied to the reactions of methyl nitrate to give quantitative information about the enthalpy and free energy balances in some of its important reactions and to enable equilibrium constants to be evaluated.

Thermochemical Properties.—(1) *Standard heat of formation of methyl nitrate.* This fundamental quantity has been the subject of only one published determination. Experiments made at Woolwich Arsenal on the heats of explosion of various substances (Whittaker, Wheeler, and Pike, *J. Inst. Fuel*, 1947, **20**, 137) gave for methyl nitrate the value :

$$Q_{\text{explosion}} = 1640 \pm 10 \text{ cal. g.}^{-1}$$

from which

$$\Delta H_f^{298} = -37.2 \pm 0.8 \text{ kcal. mole}^{-1}$$

for the heat of formation of liquid methyl nitrate. From this value and from the enthalpy differences of the elements between absolute zero and room temperature the value of the heat of formation at absolute zero of methyl nitrate, ΔH_f^0 , may be deduced :

$$\Delta H_f^0 (\text{CH}_3\text{NO}_3) = -37.200 - 8.256 + 7.443 \dagger = -39.8 \pm 0.8 \text{ kcal. mole}^{-1}$$

* S^{298} for the elements are taken from *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) as C (graphite) 1.374, 1.5H_2 46.816, 0.5N_2 2.883, and 1.5O_2 73.504, total 144.58 $\text{cal. mole}^{-1} \text{ deg. (c)}^{-1}$.

† From the following values for $H^{298.1} - H^0$ (cal.): CH_3NO_3 913.1; C (graphite) 251.56; 1.5H_2 3050.71; 1.5O_2 3104.67; 0.5N_2 1036.13; total for elements 7443.

(2) *Heat of formation of methyl nitrate vapour.* The latent heat of vaporisation of methyl nitrate has been variously reported. A recent redetermination by Moelwyn-Hughes and McKinley-McKee (*Trans. Faraday Soc.*, 1952, **48**, 247) of the variation of vapour pressure with temperature gives $L = 7730$ cal. mole⁻¹ in near agreement with the figure $L = 7800$ cal. mole⁻¹ obtained by Thomson and Purkis (*ibid.*, 1936, **32**, 674). Thus the heat of formation of gaseous methyl nitrate at 298° c is

$$\Delta H_f^{298} (\text{CH}_3 \cdot \text{NO}_3 g) = -37.2 + 7.77 = -29.4 \pm 0.8 \text{ kcal. mole}^{-1}$$

(3) *Atomic heat of formation of methyl nitrate vapour.* In explosives chemistry the correlation of molecular structure with heats of formation of compounds in their standard states from their elements in standard states has often been attempted. It has the disadvantage that the heats of formation are numerically small, and experimental errors and variations in intermolecular forces may obscure the variations due to chemical structure. The values of heats of formation of gaseous compounds from their isolated atoms, ΔH_a , form a better basis, according to Springall and Roberts (personal communication), for comparison and interpretation of behaviour.

Some of the heats of atomisation needed for the calculations are still disputed. A. G. Gaydon ("Diatomic Molecules," Chapman and Hall, London, 1947) has given $\Delta H = 103.22$ for $\text{H}_2 \rightarrow 2\text{H}$, 225.1 for $\text{N}_2 \rightarrow 2\text{N}$, and 117.2 kcal. mole⁻¹ for $\text{O}_2 \rightarrow 2\text{O}$, and Springall (*Research*, 1950, **3**, 260) has given $\Delta H = 136.1$ kcal. mole⁻¹ for $\text{C}_{\text{graphite}} \rightarrow \text{C}_{\text{gaseous}}$. Combining these with the heat of formation of gaseous methyl nitrate gives :

$$\Delta H_a^{298} (\text{CH}_3 \cdot \text{NO}_3 g) = -608.7 \text{ kcal. mole}^{-1}$$

(4) *Free energy of formation from the elements in their standard state.* From the value determined for the entropy of liquid methyl nitrate at 25° c its standard free energy of formation may be deduced from its known heat of formation.

Since $\Delta H_f^{298} = -37.2 \pm 0.800$ kcal. mole⁻¹
 and $\Delta S_f^{298} = -88.20$ cal. mole⁻¹ deg.⁻¹
 we find $\Delta F_f^{298} = -9.55 \pm 0.8$ kcal. mole⁻¹

Reaction between Methyl Alcohol and Nitric Acid and the Hydrolysis of Methyl Nitrate.—Methyl nitrate being made by esterification of methyl alcohol, it is important to know the thermodynamic functions for this reaction (no experimental work has yet been done on it). Values may be estimated for the enthalpy and free-energy changes (and hence the equilibrium constant) of the reversible reaction between pure components. By applying data obtained from measurements on the hydrolysis of methyl nitrate estimates may be made of the corresponding reaction in aqueous solution and of the energies of activation and velocity constants of esterification. At present their accuracy is limited by the accuracy of the Woolwich value 37.2 ± 0.8 kcal. for the molar heat of formation of liquid methyl nitrate.

(1) *Thermodynamic properties.* (a) Pure liquids. Inserting the values derived above and others tabulated [Nat. Bur. Standards' values quoted by H. Paul ("Principles of Chemical Thermodynamics," McGraw-Hill, New York, 1951) and F. R. Bichowsky and F. D. Rossini ("Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, 1936)] into the equation for esterification we have :

	$\text{CH}_3 \cdot \text{OH} + \text{HNO}_3 \rightleftharpoons \text{CH}_3 \cdot \text{NO}_3 + \text{H}_2\text{O}$				
Enthalpy of formation	-57.036	-41.404	-37.2	-68.317	Hence $\Delta H = -7.08$
Free energy of formation ...	-39.75	-19.10	-9.55	-56.69	Hence $\Delta F = -7.40$

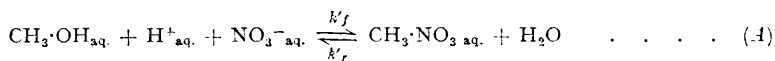
The enthalpy change on esterification is thus -7.08 ± 0.8 kcal. mole⁻¹ and should be compared with Berthelot's experimental measurement (M. Berthelot, "Sur la force des matières explosives," 1890; transl. Hake and MacNab, Murray, London, 1892) of the heat of esterification of ethyl alcohol by nitric acid, namely, 6.9 kcal. mole⁻¹.

The free energy change of -7.40 ± 0.8 kcal. mole⁻¹ corresponds to a thermodynamic

equilibrium constant K where $\log_{10} K = 5.36 \pm 0.55$, *i.e.*, $K = 2.3 \times 10^5$. Thus at room temperature the equilibrium greatly favours esterification, in accordance with the fact that Berthelot was able to prepare ethyl nitrate in virtually 100% yield at room temperature by running a stream of minute drops of ethyl alcohol into well-stirred, pure nitric acid.

(b) Aqueous solutions. If it is assumed that the enthalpy and free energy of methyl nitrate do not differ greatly from conditions of excess of water to equimolar proportions* we may evaluate the thermodynamic properties of the esterification in aqueous solutions.

In aqueous solution the nitric acid is ionised completely :



Enthalpy of formation	-58.79	-49.19	-37.2	-68.32	Hence $\Delta H = +2.46$ kcal.
Free energy of formation	...	-41.90	-26.5	-9.55	-56.69	Hence $\Delta F = +2.15$ kcal.

It will be seen that esterification is now endothermic ($\Delta H = 2.5 \pm 1$ kcal.), and that hydrolysis is favoured at room temperature ($\log_{10} K' = 2.423 \pm 0.6 = -\Delta F^\circ/RT$ corresponding to $K' = 0.0265$).

(2) *Kinetic aspects.* In any reversible reaction the ratio of the forward velocity constant k_f to the reverse k_r is equal to the equilibrium constant K ; and the difference between the apparent activation energies of forward (E_f) and reverse (E_r) reactions is equal to the enthalpy change ΔH . Thus in reaction (A) (H_2O in excess), we have $k_f'/k_r' = K'$ and $E_f' - E_r' = \Delta H'$. For this equilibrium $K' = 0.255$, and $\Delta H' = +2.46$ kcal. Moelwyn-Hughes and McKinley-McKee have investigated the hydrolysis and found values for k_r' and E_r' as functions of temperature in the range 70–140° c. Extrapolation of their results gives $E_r' = 29.5$ kcal. at 298° K, whence $E_f' = 2.5 + 29.5 = 32$ kcal. If the hydrolysis is not sensibly different in equimolar proportions and in excess of water, *i.e.*, if $E_r' = E_r$, then $E_f = -7.08 + 29.5 = 22$ kcal. The uncertainty in the value of velocity constants outside the experimental range is too great for more than an estimate of the speed of esterification. Such estimates may be made however.

At 298° K $k_r'[\text{H}_2\text{O}] \simeq 10^{-9}$ sec.⁻¹, and for the esterification between pure reactants with $K = 2 \times 10^5$ we have $k_f \simeq 4 \times 10^{-6}$ l. mole⁻¹ sec.⁻¹, or $k_f \simeq 10^{11} \exp(-22,000/RT)$ mole⁻¹ sec.⁻¹. Thus we are able from existing data and these thermodynamic measurements to predict velocities of reactions on which no experimental work has been published.

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* Equivalent to assuming zero heat of dilution of methyl nitrate from mole fraction 0.5 to 0.