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THE HEAT OF FORMATION OF AMMONIUM CARBAMATE FROM AMMONIA AND CARBON DIOXIDE

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In the synthesis of urea from ammonia and carbon dioxide, the two reactants first combine to form ammonium carbamate as follows, $2\ NH_3 + CO_2 \longrightarrow (NH_3)_2CO_2$, with the liberation of a considerable quantity of heat. The present study was undertaken with the object of obtaining an accurate measure of this heat for use in such connections as the design and control of urea synthesis apparatus. Experimental determinations of this value have previously been made,[1,2] and in addition there are available vapor-pressure data[3] from which a value may be calculated, but examination of this material revealed discrepancies which would impair its usefulness.

The experimentally determined values range from 37,700 cal. to over 42,000 cal. per mole at constant pressure. An even wider variation is encountered as shown in Table I, when the heat evolved at constant volume is calculated from existing vapor-pressure data by means of the van't Hoff equation.

TABLE I

CALCULATED HEAT OF REACTION

Temp. range, °C.	cal./g. mole Maximum	Minimum	Source of vapor-pressure data
10.0– 30.0	36,670	36,200	Naumann[3a]
14.9– 30.0	39,510	32,290	Briggs[3g]
30.0– 50.0	39,170	38,510	Naumann[3a]
30.9– 44.9	38,280	36,660	Briggs[3g]
37.8– 49.6	35,540	31,710	Isambert[3c]
49.6– 67.6	40,350	31,750	Isambert[3c]
50.0– 60.0	38,460	30,820	Naumann[3a]
77.2–114.5	45,450	37,740	Briner[3e]
114.5–152.0	42,660	36,270	Briner[3e]
152.0–197.0	46,090	22,910	Briner[3e]

It will be seen that at temperatures above 30° the results become very erratic. This is no doubt due in the first place to the difficulties in making accurate pressure determinations at elevated temperatures,

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[1] Raabe, *Rec. trav. chim.*, **1**, 158 (1882).

[2] Matignon, *Ann. chim. phys.*, [8] **14**, 24 (1908).

[3] (a) Naumann, *Ann.*, **160**, 15 (1871). (b) Horstmann, *Ann.*, **187**, 48 (1877). (c) Isambert, *Compt. rend.*, **92**, 919 (1881); **93**, 731 (1881); **94**, 958 (1882). (d) Engel and Mortessier, *ibid.*, **93**, 595, 899 (1881). (e) Briner, *J. chim. phys.*, **4**, 266 (1906). (f) Fichter and Becker, *Ber.*, **44**, 3473 (1911). (g) Briggs and Migrdichian, *J. Phys. Chem.*, **28**, 1121 (1924).

and at the pressures encountered in the case of ammonium carbamate; secondly, to the tendency of the reaction $(NH_3)_2CO_2 \longrightarrow (NH_2)_2CO + H_2O$ to take place during the time required for vapor-pressure measurements. Finally, the unknown extent of the variation from the perfect gas laws of a mixture of ammonia and carbon dioxide renders the data for the higher pressures untrustworthy.

Previous Experimental Methods.—Lecher[4] determined the heat evolved in ammonium carbamate formation by determining heats of solution and heats of neutralization, obtaining 37,700 cal. at constant pressure, as follows:

$$\begin{array}{lll}
\text{KOH aq.} + 2NH_3 \longrightarrow & \text{a cal.} & \\
\text{KOH aq.} + 2NH_3 + CO_2 \longrightarrow & \text{a} + \text{a}' \text{ cal.} & \\
\text{KOH aq.} + 2NH_3 + CO_2 + H_2SO_4 \text{ aq.} \longrightarrow & \text{a} + \text{a}' + \text{a}'' = \text{A cal.} & (1) \\
\text{KOH aq.} + H_2SO_4 \text{ aq.} \longrightarrow & \text{b cal.} & \\
\text{KOH aq.} + H_2SO_4 \text{ aq.} + (NH_3)_2CO_2 \longrightarrow & \text{b} + \text{b}' = \text{B cal.} & (2)
\end{array}$$

Combining Reactions 1 and 2

$$2NH_3 + CO_2 = (NH_3)_2CO_2 + (\text{A}-\text{B}) \text{ cal.} = 37{,}700 \text{ cal.}$$

Raabe[1] employed the direct method at one atmosphere, using a continuous flow of ammonia and carbon dioxide through a bulb contained in a calorimeter, and obtained 39,300 cal. The procedure adopted by Raabe introduced a number of sources of error, however, one of which was pointed out by Matignon,[2] namely, that some of the carbamate formed might be carried away by the exit gases and thus lead to too high a result. Moreover, the quantity of carbamate used was small (0.3–0.8 g.), the observed temperature rise, therefore, being too small for the greatest accuracy.

Matignon[2] determined the heat of solution of ammonium carbamate and the heat of neutralization of dissolved carbamate with hydrochloric acid, deducing the heat of formation of ammonium carbamate from ammonia and carbon dioxide as 39,000 cal., at constant pressure. The data required in addition to those determined by Matignon, as well as their source, were not disclosed.

The direct method possesses advantages over other means, provided such sources of error as loss or insufficiency of material can be eliminated. In the direct method as adopted in the present study, loss of material was avoided by use of a closed system; the amount of carbamate formed was approximately 5 g., the temperature rise being sufficient to minimize observational error.

Apparatus and Procedure

The principal parts of the apparatus are shown in Fig. 1. A fully charged carbon dioxide cylinder A was connected to Cylinder B so that the latter could be brought to about 41 atmospheres' (610 lbs.) gage-pressure at the beginning of each experiment. Analysis showed the presence of less than

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[4] Lecher, *Sitzb. kgl. preuss. Akad. Wiss., II.* Abth. October, **1878**.

0.03% of moisture in the carbon dioxide. Further drying of the gas was not resorted to, since some moisture is required to enable the reaction to proceed; moreover, the possible influence of the amount found above could not be greater than 100 cal. per mole of carbamate. Twelve and two-tenths meters of small copper pressure tubing led from Cylinder B to Valve F, being immersed in the form of a coil D in the constant-temperature bath C. The tubing H from Valve F to the water level in the calorimeter was insulated to minimize radiation losses at this point. The bomb I of 415cc. capacity was fitted with a valve G which could be opened or closed by means of a small key inserted through a hole in the calorimeter cover.

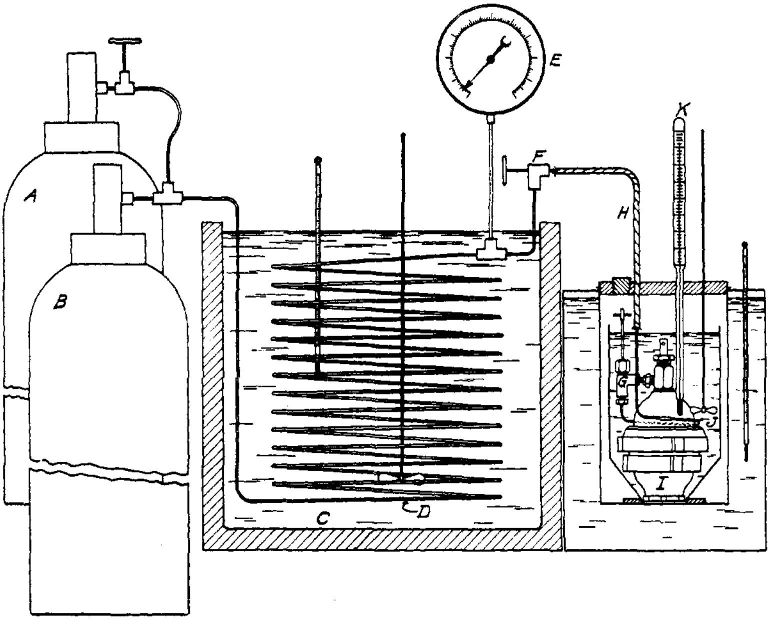

Fig. 1.

At the beginning of an experiment, the bomb was evacuated to a pressure of approximately 5 mm. of mercury, and anhydrous synthetic ammonia was admitted to a pressure of approximately 6.8 atmospheres absolute, which is about 1.7 atmospheres below saturation pressure at 21°. Higher pressures of ammonia were intentionally avoided to eliminate possible error through condensation of ammonia, and its subsequent vaporization during the determination. The bomb was then immersed in the calorimeter and connected to the carbon dioxide supply line at Valve F. The temperature of the room, the bath C, the calorimeter and the jacket having been brought to 21° ± 0.1°, the stirring rise over a preliminary period of six minutes was observed. At the end of this time, carbon dioxide was admitted by opening successively Valves F and G. To insure that the heat effect of expansion of the carbon dioxide would be reproducible in all experiments and measured in the calorimeter, the capillary tube J had been introduced as an orifice. The pressure attained equilibrium at approximately 40 atmospheres in about two minutes, Valves F and G being closed one minute later. Temperature readings were taken at 15-second intervals during the transfer period of about six minutes, after which the final cooling rate was determined. The amount of carbamate formed was determined by analysis, it being assumed on the basis of the relatively low vapor pressure of carbamate at 21° that the ammonia was completely combined in the presence of the large excess pressure of carbon dioxide employed for this purpose. The carbamate was collected under such conditions that the possibility of loss was entirely precluded, the excess of carbon dioxide being discharged and the bomb evacuated through standard acid. Water was then admitted to the bomb to dissolve the carbamate, and the solution withdrawn under vacuum with the standard acid trap in series. After several washings had been carried out in this manner to insure complete recovery, the solution of carbamate was made up to volume and analyzed for ammonia, the standard acid being back-titrated.

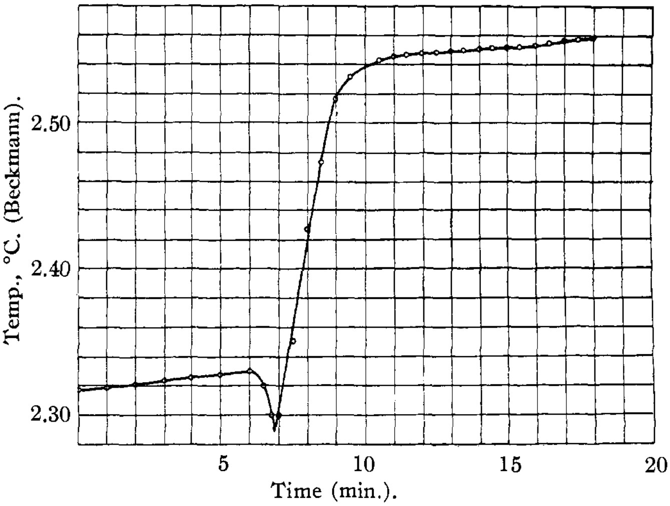

Fig. 2.—Carbon dioxide compression experiment. Initial pressure, 0.005 atmospheres (air); final pressure, 42.496 atmospheres (carbon dioxide); heat evolved, 427.0 cal.

The "water equivalent" of the complete calorimeter assembly containing 1600 g. of water was determined in a preliminary series of experiments, in which a measured amount of heat was introduced electrically. The d. c. ammeter and voltmeter used were checked against instruments of known accuracy, and during the heating period of five minutes these instruments were read at five-second intervals. The values obtained in four experiments ranged from 2071 to 2078 g. of water, or an average of 2075.

In a second series of preliminary experiments, the heat effect of the introduction of the carbon dioxide into the calorimeter bomb was measured in the absence of ammonia. For this purpose, the bomb was evacuated, immersed in the calorimeter and carbon dioxide was admitted to a pressure of 40 atmospheres' gage, the technique being identical with that to be used in later experiments with ammonia present. It was realized that in the later experiments with ammonia present, the total amount of carbon dioxide entering the bomb would include the additional quantity required to react with the ammonia. This correction was subsequently calculated, for it could not be determined directly. The temperature rise observed in three experiments[5] was 0.202, 0.204 and 0.207°, or an average of 0.205°, corresponding to the liberation of 427 cal. Fig. 2, which typifies these experiments, clearly shows the initial temperature drop due to the Joule-Thomson effect taking place within the calorimeter. It is interesting to note that the above value of 427 cal. is in good agreement with that obtained from theoretical considerations, which was 448 cal. This latter value was arrived at by calculating the Joule-Thomson effect at the orifice and the heat of compression in the bomb.

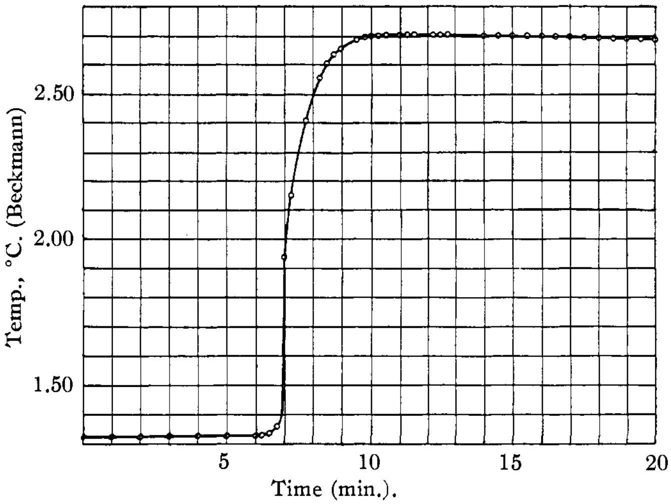

Fig. 3.—Expt. 14. Heat of reaction, $2NH_3 + CO_2 \longrightarrow (NH_3)_2CO_2$; initial pressure, 7.122 atmospheres (ammonia); final pressure, 42.633 atmospheres (carbon dioxide).

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[5] For convenience, these experiments will be referred to as carbon dioxide blanks.

Experimental Data and Method of Calculation

Table II and Fig. 3 present the time, temperature and other observations taken during a determination of the heat of reaction (Expt. 14). This material will be used to illustrate the procedure followed in the final calculations.

TABLE II

HEAT OF REACTION DATA (EXPT. 14)

Time, Min.	sec.	Observed temp., °B.[d]	Time Min.	sec.	Observed temp., °B.	Time, Min.	sec.	Observed temp., °B.	Time Min.	sec.	Observed temp., °B.
0		1.323	8		2.495	11	30	2.705	15		2.699
1	0	1.324		15	2.558		45	2.705		30	2.698
2	0	1.325		30	2.604	12		2.705	16		2.697
3	0	1.326		45	2.636		15	2.705		30	2.696
4	0	1.327	9		2.659		30[c]	2.704	17		2.694
5	0	1.328		15[b]	...		45	2.704		30	2.693
6	0	1.330		30	2.685	13		2.703	18		2.691
	15[a]	...		45	2.694		15	2.703		30	2.690
	30	1.37	10		2.697		30	2.702	19		2.690
	45	1.64		15	2.700		45	2.701		30	2.688
7		1.94		30	2.704	14		2.700	20		2.687
	15	2.15		45	2.704		15	2.700			
	30	2.30	11		2.704		30	2.699			
	45	2.41		15	2.704		45	2.699			

[a] Valve opened (beginning of transfer period).

[b] Valve closed.

[c] End of transfer period.

[d] Beckmann thermometer readings.

The heat evolved by the formation of the carbamate may be expressed by the following equation, which takes into account the necessary corrections.

Heat evolved $= (A + B)(x + y + z) - C(x + y) - D = (1.345 + 0.0025)(2075 + 8.24 + 2.42) - 0.205(2075 + 8.24) + 26.3 = 2409.6$ cal., where A is the temperature rise of the transfer period after correction of the Beckmann readings for deviation of the latter from a Bureau of Standards compared thermometer;

B is the Regnault-Pfaundler cooling correction $= T_{\mathrm{tr}}\left[V_p + \frac{V_c - V_p}{\Theta_c - \Theta_p}(\Theta_{\mathrm{tr}} - \Theta_p)\right] = 6.25\left[-0.00117 + \frac{0.00217 + 0.00117}{2.694 - 1.326}(2.380 - 1.326)\right] = +0.0025°$;

T_{tr} is the time of the transfer period in minutes;

V_p, the cooling rate of preliminary period;

V_c, the cooling rate of final period;

Θ_c, the mean temperature of final period;

Θ_p, the mean temperature of preliminary period;

Θ_{tr}, the mean temperature of transfer period;

C is the temperature rise (corrected as for A) of the transfer period in the carbon dioxide blank;

D, the Joule-Thomson effect in calories of that part of the carbon dioxide which enters into the reaction to form carbamate $= \Delta T N_1 Cp_{\mathrm{CO_2}} = \mu N_1 Cp_{\mathrm{CO_2}}(P - P_0) = (-1.15)(0.0665)(8.79)(42.8 - 3.7) = -26.3$ cal.;

T is the change in temperature in °C. of the carbon dioxide expanding through orifice J from mean effective pressure P of the carbon dioxide, at the source, against the mean pressure (P_0) of the ammonia in calorimeter bomb $= \mu(P - P_0) = -45°$;

μ = Joule-Thomson coefficient for carbon dioxide = —1.15° per atmosphere;

N_1 = number of moles of entrant carbon dioxide combining to form carbamate;

$Cp_{CO_2} = 7.0 + 0.0071\ T + 0.00000186\ T^2 = 8.79$ cal. = molal heat capacity of carbon dioxide at mean of calorimeter and entrant gas temperatures;

x = heat capacity of the calorimeter assembly as determined = 2075 g. cal. per deg.;

y = heat capacity of the carbon dioxide in bomb (in excess of that required for the reaction) $= N_2 \underset{295}{Cp_{CO_2}} = (0.922)(8.93) = 8.24$ g. cal./deg.;

N_2 = number of moles of carbon dioxide in excess of that required for the reaction (from van der Waals' equation of state);

Cp = molal heat capacity of carbon dioxide at 22°.

z = heat capacity of the carbamate formed $= N_3 Cp_{(NH_3)_2CO_2} = 0.0665\ (36.4) = 2.42$ g. cal./deg.;

N_3 = number of moles of carbamate formed = 0.0665;

$Cp_{(NH_3)_2CO_2}$ = molal heat capacity of carbamate calculated from the molal heat capacities of the elements using the values C = 1.8, H = 2.3, O = 4.0, N = 6.4, assigned by Kopp[6] = 36.4 g. cal./mol./deg.

The 2409.6 cal. found as above is referred to the quantity of carbamate found by analysis, which in this case was 1.8624 g. of nitrogen, equivalent to 5.1892 g. or 0.0665 mole of carbamate; from which we obtain $\Delta U_v = 2409.6/0.0665 = 36{,}250$ cal. Five determinations gave the following results: 36,340, 36,350, 36,100, 36,250 and 36,480 cal., or an average of 36,300 cal.

The heat of reaction at constant pressure may be calculated from the above-determined value by the usual equation $\Delta U_p = \Delta U_v - \Delta nRT$, where Δn is the difference between the final and initial number of gas moles involved. The value thus obtained is 38,060 cal.

Summary

The heat of formation of ammonium carbamate from ammonia and carbon dioxide has been determined as 36,300 cal. per mole of carbamate at constant volume. This value, which was obtained by the direct method, is appreciably lower than previous experimental values, with the exception of Lecher's result of 37,700 cal. at constant pressure. It may also be noted that the value calculated from Naumann's vapor-pressure data in the range where accuracy of the latter might be expected (10–30°) is in good agreement with the results of the present study.

WASHINGTON, D. C.

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[6] Kopp, *Ann. Chem. Pharm. Supp.*, [1] 3, 289 (1864).