probable trend of the critical curve of the mixture starting at the critical point of ammonia, rising to a very high pressure and finally curving back to end at the critical temperature $t_c = -147.1°$ and pressure $p_c = 33.5$ atmospheres of nitrogen. A number of constant composition curves for the liquid phase have also been drawn, the numerical values of which are given in Table IV. The data were obtained graphically. For illustration the "200," "250" and "300" composition curves have been extrapolated roughly to show the possible trend of the vapor branch. These extrapolations are of course highly qualitative. The curves for the other compositions will likewise come down and make contact of the first order with the critical curve (envelope), in somewhat the fashion depicted. The shape of the curves seems to indicate retrograde condensation of the first kind.[4]

TABLE IV

TEMPERATURES AT CONSTANT COMPOSITION IN °C.

Pressure, atm.	Composition in cc. N_2 (S. T. P.) per g. liquid ammonia 100	150	200	250	300
325	76.4	90.4	96.6	100.6[a]	
400	68.4	82.1	89.8	94.2[a]	96.6[a]
500	62.0	74.8	82.1	86.6	89.6
550	60.0	72.5	79.2	83.5	86.2
600		70.3			
800		65.3	72.9	77.5[a]	
1000		63.0	70.8	75.5[a]	

[a] These values are rather uncertain.

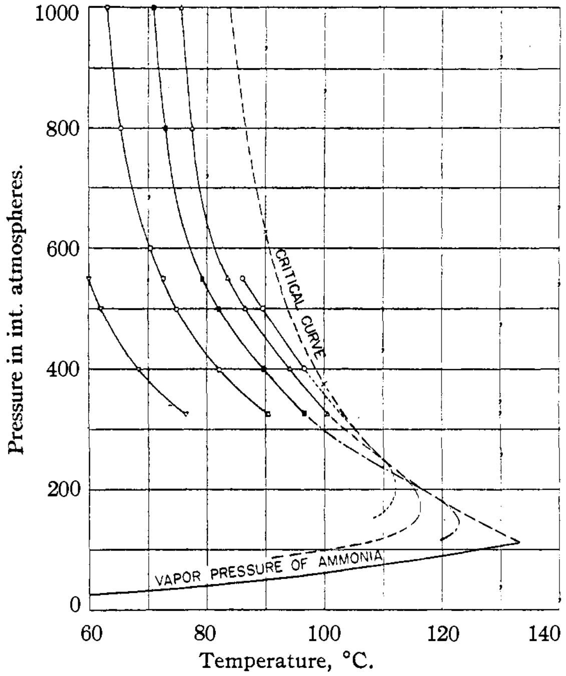

Fig. 5.—Constant composition curves and critical curve for nitrogen-ammonia mixtures, N_2 (S. T. P.) per g. of NH_3: ▽, 100 cc.; □, 150; ⊠, 200; △, 250; ○, 300.

Summary

The solubility of hydrogen in liquid ammonia was determined at 0° and at pressures to 1000 atmospheres. Over the same pressure range the solubility of nitrogen was measured at 0, 50, 75, 90 and 100°. Two critical points, one at 90° and about 600 atmospheres, the other at 100° and approximately 375 atmospheres, were found. The probable trend of the critical curve was sketched over a short range.

WASHINGTON, D. C. RECEIVED JULY 9, 1937

---

[4] For full discussion see, *e. g.*, Kuenen, "Theorie der Verdampfung und Verflüssigung von Gemischen," Joh. Ambrosius Barth, Leipzig, 1906.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

Thermodynamics of Lead Iodide[1]

BY JESSIE Y. CANN AND ALICE C. TAYLOR

The purpose of this investigation is to determine, by means of electromotive force measurements, the free energy of formation, ΔF, the change of entropy, ΔS, and the change in heat content, ΔH, of lead iodide.

In contrast to some previous investigators, *e. g.*, Gerke[2] who used 1 and 0.1 *M* solutions of electrolytes, we have used 0.1, 0.05 and 0.025 *M* solutions. Taylor[3] and Taylor and Perrott[4] have also studied lead iodide.

Method and Apparatus.—In this investigation the cell

$PbHg_x$, $PbI_2(s)$, $PbI_2(satd.) + m$ KI(aq.), AgI(s), Ag(s)

was measured. Pyrex H-tubes were employed, similar to those used by Gerke.[2]

The cell was placed in the usual oil thermostat, regulated at 25°, and measurements were made

---

[1] The experimental part of this paper is a portion of a thesis submitted by A. C. Taylor in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

[2] Gerke, THIS JOURNAL, **44**, 1684 (1922); and *Chem. Rev.*, **1**, 337 (1925).

[3] Taylor, THIS JOURNAL, **38**, 2295 (1916).

[4] Taylor and Perrott, *ibid.*, **43**, 489 (1921).

with a shielded Leeds and Northrup Type K potentiometer.

Materials.—All solutions were made up by weight, moles per 1000 g. of water in vacuum, from high grade "analyzed" salts and conductivity water. Care was taken to remove all traces of oxygen by bubbling an inert gas through the solutions.

The lead used for the amalgam electrodes was Baker Analyzed Granulated with a maximum impurity of 0.005% iron.

The lead amalgam electrodes were made according to the method of Randall and Cann,(5) and Cann and Sumner.(6)

The silver iodide electrodes were made according to the methods of Cann and Taylor.(7)

The procedure employed was that described previously.(5–7)

Experimental Results

Twelve cells were made up. Saturated solutions of lead iodide in potassium iodide were made by shaking a large excess of lead iodide in small amounts of the potassium iodide solutions of different molalities, and allowing the solutions to stand for two weeks with occasional agitation. Readings were taken, at first, every half hour on alternate days, while the cells remained at equilibrium for over two months at 25°. At the end of this time, the temperature was increased, by 5° intervals, to 40°. Each temperature was maintained for at least two weeks, and readings taken daily. Then the temperature was decreased gradually, stopping at irregular intervals for a few days, and readings taken each day. All of the cells came to equilibrium in a day or two; and there was no apparent difference caused by the two varieties of silver iodide electrodes. Six of the cells were discarded at various stages throughout the investigation because examination disclosed that oil from the thermostat had seeped in causing erratic readings.

TABLE I

The Cell: $PbHg_x$, $PbI_2(s)$, PbI_2(satd.) + m KI(aq.), AgI(s), Ag(s).

Temp., °C.	0.1 *m* Cell 1a	0.1 *m* Cell 1b	0.1 *m* Cell 1c	0.05 *m* Cell 2a	0.05 *m* Cell 2c	0.025 *m* Cell 3b
15.30	0.20940	0.20892	0.20925	0.20955	0.20945	0.21043
17.00	.....	.....	.....	.20920	.20905	.....
18.70	.20854	.20785	.20800	.....	.....	.....
23.60	.20785	.20735	.20720	.20772	.20795	.20845
25.00	.20705	.20700	.20699	.20745	.20750	.20810
26.10	.20720	.20684	.20660	.20720	.20720	.20708
27.50	.20670	.....	.....	.....	.....	.....
30.00	.20535	.20590	.20575	.20650	.20605	.20760
32.10	.....	.....	.....	.....	.....	.20623
32.20	.20660	.20590	.20570	.20620	.20635	.....
35.00	.20480	.....	.20445	.20535	.20525	.20515
36.00	.20499	.20515	.20470	.20530	.20533	.....
40.00	.20375	.20330	.20360	.20445	.20424	.....

Averages of ten or more readings at the various temperatures for the different cells kept are listed in Table I. Deviations from the average were never more than two or three-tenths of a millivolt. A plot of all values obtained shows that the slope of the curve, $\Delta E/\Delta T$, is -0.0002. The maximum deviation from this value was ± 0.00006.

The chemical reaction involved in this cell is

$$(1 + a)PbHg_x(s) + 2AgI(s) = PbI_2(s) + 2Ag(s) + aPbHg_y(l)$$

Since there is less likelihood of complex formation in 0.05 molal potassium iodide than in 0.1 *m*, and since cells 2a and 2c gave the most uniform results, we take the value for E^0 at 25° for the cell reaction as 0.2075 v. This gives $\Delta F^0 = -NFE = -9576$ cal.

Discussion of Results

Combining the above value with the change in free energy for the electrode reactions, thus

$$\begin{array}{ll}
PbHg_x + 2AgI = xHg + PbI_2 + 2Ag; & \Delta F^0 = -9576 \\
Pb(s) + xHg = PbHg_x; & \Delta F^0 = -263^{2} \\
\hline
Pb(s) + 2AgI = PbI_2 + 2Ag; & \Delta F^0 = -9839 \\
Ag(s) + I_2 = 2AgI; & \Delta F^0 = -31{,}640^{8,2} \\
\hline
Pb(s) + I_2 = PbI_2; & \Delta F^0 = -41{,}479
\end{array}$$

we obtain the change in free energy for the formation of lead iodide from its elements as $-41{,}479$ cal. Gerke's value is $-41{,}501$.

Since we know that

$$-NF\frac{dE}{dT} = -\Delta S = \frac{-NFE - \Delta H}{T}$$

we can next calculate the change in heat content for the cell reaction. This we find to be $-12{,}327$ cal. In order to obtain the change in heat content, ΔH, for lead iodide from its elements, we combine the reactions

$$\begin{array}{ll}
PbHg_x + 2AgI = xHg + PbI_2 + 2Ag; & \Delta H = -12{,}327 \\
Pb(s) + xHg = PbHg_x; & \Delta H = -42^{2} \\
\hline
Pb(s) + 2AgI = PbI_2 + 2Ag; & \Delta H = -12{,}369 \\
2Ag(s) + I_2 = 2AgI; & \Delta H = -29{,}890^{9} \\
\hline
Pb(s) + I_2 = PbI_2; & \Delta H = -42{,}259
\end{array}$$

If we use Noyes and Freed's[10] value for ΔH for silver iodide, *i. e.*, $-29{,}920$, we get ΔH for the

---

(5) Randall and Cann, THIS JOURNAL, **52**, 589 (1930).

(6) Cann and Sumner, *J. Phys. Chem.*, **36**, 2615 (1932).

(7) Cann and Taylor. THIS JOURNAL, **59**, 1484 (1937).

(8) "International Critical Tables," McGraw-Hill Book Co., Inc., New York City, 1930, Vol. VII, p. 268.

(9) Ref. (8), Vol. V, p. 188.

(10) Noyes and Freed, THIS JOURNAL, **42**, 476 (1920).

change in heat content of lead iodide as −42,289. And if we use Jones and Kaplan's[11] value for ΔH for silver iodide, *i. e.*, −28,708, we get ΔH for the change in heat content of lead iodide as −41,077. Gerke's value is −41,859.

From $NF(\mathrm{d}E/\mathrm{d}T) = \Delta S$ we calculate the change in entropy, ΔS, for the cell reaction to be −9.23 cal. In order to obtain the change in entropy, ΔS, for lead iodide from its elements, we combine the following reactions

$$\mathrm{PbHg}_x + 2\mathrm{AgI} = x\mathrm{Hg} + \mathrm{PbI_2} + 2\mathrm{Ag}; \quad \Delta S = -9.23$$

$$\mathrm{Pb(s)} + \mathrm{Hg} = \mathrm{PbHg}_x; \quad \Delta S = +0.74^{2}$$

$$\mathrm{Pb(s)} + 2\mathrm{AgI} = \mathrm{PbI_2} + 2\mathrm{Ag}; \quad \Delta S = -8.49$$

$$2\mathrm{Ag(s)} + \mathrm{I_2} = 2\mathrm{AgI}; \quad \Delta S = +9.60^{11}$$

$$\mathrm{Pb(s)} + \mathrm{I_2} = \mathrm{PbI_2}; \quad \Delta S = +1.11$$

Gerke[2] reports −1.20 for ΔS for lead iodide.

If now we use the third law, $\Delta F = \Delta H - T\Delta S$, using our values of $\Delta F = -41{,}479$ and $\Delta S = +1.11$, we obtain for ΔH the value −41,148. If next we use the value of Lewis and Randall,[12] $\Delta S = 6.8$ for 2AgI, with the above equations, we obtain ΔS for lead iodide from its elements as −1.69. Using this value with the third law, and our value $\Delta F = -41{,}479$, we obtain ΔH for lead iodide as −41,983.

We take as our values for lead iodide from its elements: $\Delta F = -41{,}479$; $\Delta H = -42{,}259$ and $\Delta S = 1.11$.

Summary

We have calculated the values of ΔF, ΔH and ΔS for the formation of lead iodide from its elements. We have also compared various calculations made from available data in the literature.

NORTHAMPTON, MASS. RECEIVED APRIL 5, 1937

(11) Jones and Kaplan, THIS JOURNAL, **50**, 1845 (1928).

(12) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, p. 451.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Azomethane. II. The Effect of Temperature

BY MILTON BURTON,(1) THOMAS W. DAVIS AND H. AUSTIN TAYLOR

In a previous report(2) evidence was presented indicating that the photolysis of azomethane is not to be represented by the over-all equation

$$\mathrm{CH_3N{=}NCH_3} + h\nu \longrightarrow \mathrm{C_2H_6} + \mathrm{N_2} \qquad (1)$$

On the other hand, there was no evidence that the primary step may be represented entirely by the equation

$$\mathrm{CH_3N{=}NCH_3} + h\nu \longrightarrow \mathrm{N_2} + 2\mathrm{CH_3} \qquad (2)$$

We have shown that the gaseous products not soluble in hydrochloric acid contain approximately 55% nitrogen, 3% methane and 42% ethane when the photolysis is permitted to proceed to a 10% pressure increase at a temperature of 20°. These results and others reported are consistent with the ideas that there is a secondary reaction between free methyl radicals and azomethane and that some of the azomethane may decompose by a rearrangement process to yield ultimate molecules in one primary act, as shown by equation 1. The first idea has been justified further by a study of the effects of temperature. The results are reported herein.

The assumption hitherto has been that equation 1 represents in a rough way the principal course of the reaction even at high temperatures. We have now found this assumption to be absolutely unjustified. It is shown that as the temperature is increased the yield of ethane decreases markedly, methane becoming the chief hydrocarbon product.

Experimental Method

The procedure employed was similar to that hitherto reported.(2) The azomethane sample used throughout this work was a portion from the previous investigation. An air thermostat with Pyrex window was substituted for the water thermostat previously used. The temperature within the thermostat varied within a range of 2.5°. In the following statements the average temperature is reported.

As in the previous work,(2) there was interposed between the light source(3) and the reaction system a Corning No. 534 blue ultra filter which, according to the specifications, transmits only wave lengths longer than 3500 Å. This filter was used in all the experiments; the distance of the arc from the wall of the reaction vessel was rigidly fixed at 10.2 cm. As before, the total thickness of Pyrex between the arc and the reacting gas was of the order of 2 mm.

Photolysis of Azomethane.—The initial pressure of azomethane was fixed arbitrarily at approximately 100

---

(1) Present address: Department of Chemistry, University of California, Berkeley, Calif.

(2) Burton, Davis and Taylor, THIS JOURNAL, **59**, 1038 (1937).

(3) Burton, *ibid.*, **58**, 1645 (1936).