[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA[1]]

The Decomposition of Silver Nitrite

BY MERLE RANDALL, GEORGE G. MANOV[2] AND OLIVER L. I. BROWN[3]

The heat capacities of all the substances involved in the reaction

$$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g) \quad (1)$$

are known from very low temperatures to temperatures in the neighborhood of 420°K. where the equilibrium pressure of nitric oxide can be measured. We may, therefore, calculate the heat of the reaction with fair certainty and obtain a good extrapolation of the free energy to our standard reference temperature. The reaction also affords the opportunity of comparing three important methods of treating equilibrium data.

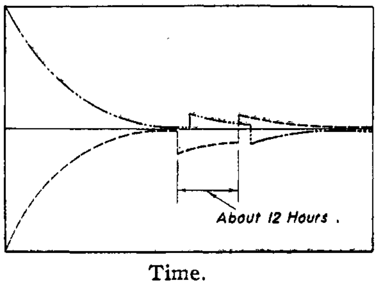

Fig. 1.

The measurements of this equilibrium also furnish us with important data for the interpretation of the older measurements used in the calculations of the thermodynamic properties of nitrate and nitrite ion. Several investigators[4] have measured the equilibrium when nitric oxide is bubbled through aqueous nitric acid. Abel, Schmid and Simon[5] studied the equilibrium when metallic silver is treated with nitric acid and Lewis and Adams[6a] and Abegg and Pick[6b] have studied the equilibrium pressure of nitric oxide over aqueous solutions of silver nitrate saturated with silver nitrite and silver. For these reactions the chief source of uncertainty in the evaluation of the standard free energies is due to uncertainties in the activity coefficients of the ions and the heats of the reactions.

Experimental

Preparations A_1 and A_2 were pure silver nitrite, A_3 and A_4 were pure silver nitrite mixed with a little finely divided silver nitrate and silver; B_1 and B_2 were pure finely divided silver nitrate and silver, and B_3 contained also a little pure finely divided silver nitrite. Preparations A_1 and B_1, A_2 and B_2, etc., were measured in pairs. No difference in behavior as between Series A_1, A_2, A_3, and A_4 and between B_1, B_2, and B_3 was noted.

The salts were weighed into a vertical reaction tube, approximately 12 cm. long by 4 cm. in diameter, connected to an empty manometer. For the A series 0.153 mole of silver nitrite was used, this amount having been calculated from the results of preliminary experiments to correspond to less than 10% decomposition at the highest temperature employed. Similarly, the amounts of silver and silver nitrate for the reverse reaction were so chosen that at the lowest equilibrium pressure, the synthesis of silver nitrite would be less than 10% complete. The reaction vessels were evacuated separately at room temperature by means of a mercury vapor pump for three days. At the end of this period mercury was admitted to the manometers, and the reaction vessels heated by means of an oil thermostat which could be set to operate at various temperatures.

At the lowest temperature, 101.6°, the equilibrium pressure of nitric oxide was established in less than twenty-four hours and was found to be 0.249 atmosphere from the decomposition or forward reaction, and 0.245 atmosphere from the reverse or synthesis reaction, Series A_1 and B_1. The pressure of nitric oxide was then artificially displaced from equilibrium by putting a slightly reduced pressure on the manometer of the vessel containing A_1 and a slightly increased pressure on the manometer of the vessel containing B_1. After twelve hours the "open" ends of the manometers were opened to the atmosphere, and the reactions allowed to proceed to equilibrium. The final pressures were practically identical with those found above. The time–pressure cycle is illustrated in Fig. 1. This cycle was repeated for most of the points and the average of each taken for the forward and reverse reactions, respectively. The temperature was then raised and the process repeated. By this device, equilibrium was isothermally approached from both sides for each preparation.

In the later series, the temperature of the oil-bath was changed so that each equilibrium point was approached from the low and the high temperature side. No difference was observed in the final equilibrium pressure by the two methods.

In the first series, it was found that the pressures of nitric oxide obtained in the forward and reverse reactions were nearly the same up to 400°K., but that above this

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[2] Present address: U. S. Dept. of Commerce, National Bureau of Standards, San Francisco, California.

[3] Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[4] (a) Abel, Schmid and Babad, *Z. physik. Chem.*, **136**, 135 (1928); (b) Klemenc and Hayek, *Z. anorg. allgem. Chem.*, **186**, 181 (1930); (c) Lewis and Edgar, THIS JOURNAL, **33**, 292 (1911).

[5] Abel, Schmid and Simon, *Z. Elektrochem.*, **37**, 626 (1931).

[6] (a) Lewis and Adams, THIS JOURNAL, **37**, 2308 (1915); (b) Abegg and Pick, *Z. anorg. Chem.*, **51**, 1 (1906).

temperature the equilibrium pressure of nitric oxide over silver and silver nitrate varied only slightly with temperature. Another identical set of reaction vessels was prepared, A_2 and B_2, and the experiments repeated with great care. The break in the temperature–pressure curve was found to be reproducible, and at the same time the rate of attainment of equilibrium was found to be slower. The silver nitrate was found to have sintered. In no case was there visual evidence of nitrogen peroxide. A small tube attached to the manometer was surrounded by solid carbon dioxide thus decreasing the pressure of the nitric oxide. When the reaction had again proceeded to equilibrium, the same pressure was attained, thus indicating that the gas phase was pure nitric oxide.

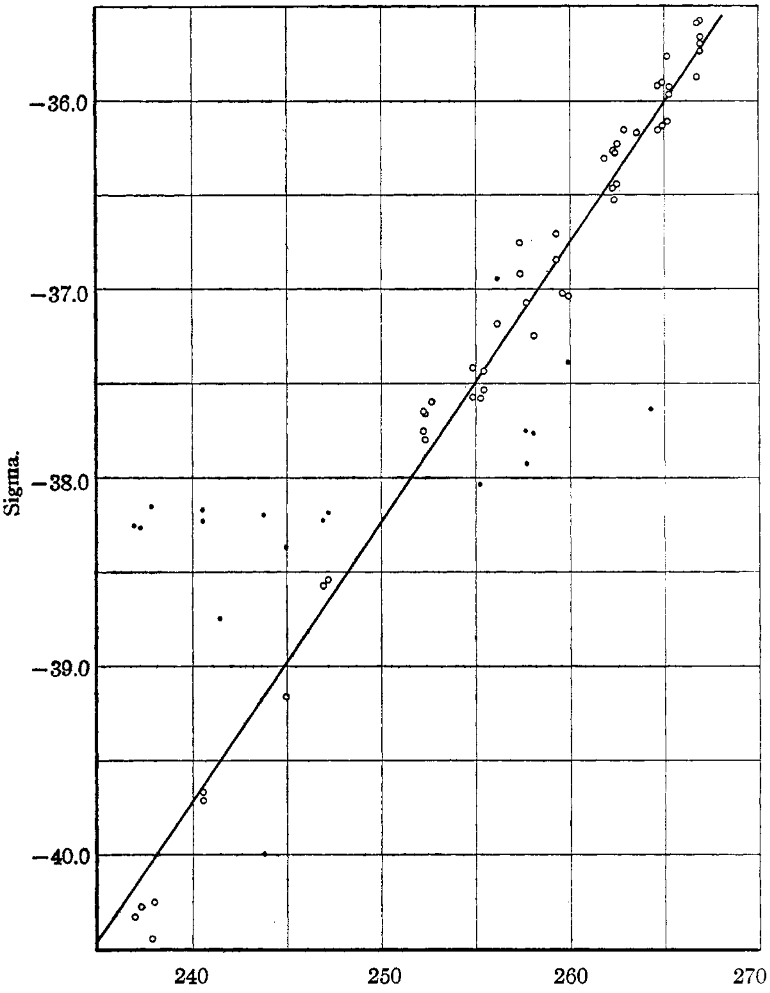

Fig. 2.—$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g)$.

The most probable explanation of the anomalous points is that solutions of silver nitrate and silver nitrite formed at the higher temperatures. When we are dealing with a solid phase which is mostly (95%) silver nitrite, the effect of solution is small, as the points representing a function of the equilibrium pressure of nitric oxide with temperature continue to fall on an extension of the straight line previously obtained. When the solid phase consists mostly (95%) of silver nitrate and silver, anomalies occur above 400°K. If the amount of silver nitrite synthesized is small its activity in a solution would be low, and this would qualitatively explain a lower equilibrium pressure of nitric oxide. In the last series, approximately equal parts of silver, silver nitrate, and silver nitrite were used. The resulting point (67B+) fell between the points for the A and B series, at a temperature of 414.1°K. Many attempts were made without avail to write reactions for which the change in heat content would correspond to that indicated by the slope of the $-R \ln P$ *versus* $1/T$ curve for the anomalous points. Since we are interested primarily in the case in which solutions are absent, and in view of the later agreement of the accepted values with independent measurements, we feel justified in giving no weight to the points obtained in the synthesis or B series above 400°K. Such discarded points are indicated by dots in Fig. 2.

Correlation of Results

The activity of silver nitrite, of solid silver and silver nitrate may be taken as unity because we found no significant difference in the measured pressure when we had a small amount of silver and silver nitrate in contact with a large amount of silver nitrite and in the case when we had a small amount of silver nitrite on the surface of a large amount of silver and silver nitrate. The evidence for this conclusion has just been presented. The activity or the fugacity of nitric oxide may be set equal to its pressure in atmospheres. Instead of tabulating the values of the pressure we give in Table I all the recorded values of $-R \ln K$ which is equal to $-4.575 \log P(\mathrm{NO})$. In the first column we have indicated the number of the run, the letters A and B referring to the preparation mentioned in the previous section.

Method I.—In accordance with the method suggested by Lewis and Randall[7] we have plotted the value of sigma defined by the equation

$$\Sigma = \Delta H°_0/T + I = -R \ln K - 6.95 \ln T + 0.00694T + 0.00000091T^2 \quad (2)$$

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[7] (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., Exercise 6, p. 300; (b) Randall and Mohammad, *Ind. Eng. Chem.*, **21**, 1048 (1929).

TABLE I

$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g)$

	T	$-R \ln K$		T	$-R \ln k$
1A$_1$+	388.6	1.848	34B$_2$+	381.3	2.266
2B$_1$−	388.6	1.682	35A$_2$−	381.0	2.086
3A$_1$+	392.4	1.072	36B$_2$−	381.0	2.298
4B$_1$+	392.4	1.226	37A$_2$−	381.2	2.005
5A$_1$−	391.5	1.100	38B$_2$−	381.2	2.257
6B$_1$+	391.5	1.197	39A$_2$+	385.7	1.731
7A$_1$+	415.7	−0.845	40B$_2$+	385.7	1.867
9A$_1$+	415.7	− .821	41A$_2$+	396.5	0.934
11A$_1$+	421.5	−1.361	42B$_2$+	396.5	1.037
13A$_1$+	422.1	−1.410	43A$_2$+	396.5	0.888
17A$_1$+	420.5	−1.541	44B$_2$−	396.4	1.028
19A$_2$+	374.7	2.765	45A$_2$+	405.0	0.198
20B$_2$−	374.7	2.797	47A$_2$−	404.6	.221
21A$_2$−	374.7	2.724	50B$_2$−	390.4	1.436
22B$_2$+	374.7	2.884	51A$_3$+	385.3	1.552
23A$_2$−	374.9	2.584	52A$_3$+	384.8	1.530
24B$_2$+	374.9	2.873	54A$_3$+	391.8	1.059
25A$_2$+	377.0	2.518	56A$_3$−	387.5	1.346
26B$_2$+	377.0	2.555	58A$_3$+	408.3	−0.360
27A$_2$+	377.1	2.375	62A$_4$+	388.1	1.529
28B$_2$+	377.1	2.723	63A$_4$−	379.4	2.341
29A$_2$+	377.5	2.358	64A$_4$+	395.8	1.086
30B$_2$−	377.5	2.584	65A$_4$−	382.0	2.233
31A$_2$−	377.8	2.341	66A$_4$−	380.4	2.367
32B$_2$−	377.8	2.574	69A$_2$+	420.3	−1.346
33A$_2$+	381.3	2.064			

against the reciprocal of the absolute temperature. The values of the coefficient of the ln T, T, and T^2 terms were taken by properly summing the following heat capacities.

$$AgNO_2(s);^{8}\ S^\circ_{298.1} = 30.62 \text{ cal. per mole per deg.}; \quad C_p = 18.87 \qquad (3)$$

$$Ag(s);^{9}\ S^\circ_{298.1} = 10.20 \text{ cal. per mole per deg.}; \quad C_p = 5.60 + 0.0015T \qquad (4)$$

$$AgNO_3(s);^{10}\ S^\circ_{298.1} = 33.68 \text{ cal. per mole per deg.}; \quad C_p = 17.45 + 0.016T \qquad (5)$$

$$NO(g);^{11}\ S^\circ_{298.1} = 50.34 \text{ cal. per mole per deg.}; \quad C_p = 7.74 - 0.00362T + 0.00000546T^2 \qquad (6)$$

We chose $\Delta H^\circ_0 = 14{,}819$ whence we have the average value of $I = -75.258 \pm 0.134$.

We thus have an equation

$$\Delta F^\circ_T = 14{,}819 + 6.95\ T \ln T - 0.00694\ T^2 - 0.0_691\ T^3 - 75.258\ T$$
$$\Delta F^\circ_{298.1} = 3550 \text{ cal. per mole}; \ \Delta H^\circ_{298.1} = 13{,}412 \text{ cal. per mole}; \ \Delta S^\circ_{298.1} = 33.083 \text{ E. U. (Method I)} \qquad (7)$$

We might, perhaps, have chosen a slightly smaller value of ΔH°_0 but the variations of I based on our value seem to be random, thus showing that Equation 7 may be used to reproduce the data between the temperatures of the measurements.

Method II.—Method I assumes only the empirical algebraic heat capacity equations and the form of the equation, determining both the algebraic constants ΔH°_0 and I from the data alone. Now summing the entropies given in Equations 3 to 6 we find $\Delta S^\circ_{298.1} = 32.98$ E. U. in fair agreement with 33.100 given by Method I in Equation 7. By means of the equation[7a] (p. 453)

$$I = \Delta S^\circ_T + \Delta C^\circ_p\ (1 + \ln T) + \Delta C_p{}'T + 1/2\ \Delta C_p{}''\ T^2 \qquad (8)$$

we find $I = -75.147$, and combining the values of sigma we find $\Delta H^\circ_0 = 14{,}775 \pm 53$ cal. per mole. We thus have the algebraic equation

$$\Delta F^\circ_T = 14{,}775 + 6.95\ T \ln T - 0.00694\ T^2 - 0.0_691\ T^3 - 75.147\ T; \ \Delta F^\circ_{298.1} = 3537 \text{ cal. per mole}; \ \Delta H^\circ_{298.1} = 13{,}368 \text{ cal. per mole}; \ \Delta S^\circ_{298.1} = 32.98 \text{ E. U.} \quad \text{(Method II)} \qquad (9)$$

Equation 9 gives a good representation of the data when the algebraic heat capacity equations are required.

Method III.—The method suggested by Giauque,[12] which does not make any algebraic approximations, can be used in this instance because the heat capacity curves of all the substances are known from very low temperatures. Values of the function $((F^\circ - H^\circ_0)/T)$ for each of the solid substances may be calculated by graphically evaluating areas, thus

$$\frac{F^\circ - H^\circ_0}{T} = \frac{H^\circ}{T} - \frac{H^\circ_0 - S^\circ}{T} = \frac{1}{T}\int_0^T C_p\,\mathrm{d}T - \int_0^T C_p\,\mathrm{d}\ln T \qquad (10)$$

We have used the same algebraic representations for the heat capacities above 25°, as are given by Equations 3, 4, and 5. For nitric oxide the data of Johnston and Chapman[11] were used. The values at several round temperatures and for $\Delta(F^\circ - H^\circ_0)/T$ are given in Table II.

TABLE II

VALUES OF THE FUNCTION $(F^\circ - H^\circ_0)/T$

T, °K.	Ag(s)	$AgNO_2(s)$	$AgNO_3(s)$	NO(g)	$\Delta(F^\circ - H^\circ_0)/T$
298.1	−5.586	−17.048	−18.647	−42.985	−33.122
300	−5.616	−17.134	−18.743	−43.033	−33.124
350	−6.346	−19.284	−21.151	−44.163	−33.092
400	−7.003	−21.234	−23.370	−45.141	−33.046
450	−7.601	−23.014	−25.428	−45.999	−33.000

Interpolating for the several temperatures we find

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[8] The heat capacity of silver nitrite was determined in this laboratory by Brown, Smith and Latimer, THIS JOURNAL, **59**, 921 (1937).

[9] (a) Giauque and Meads, unpublished; (b) see compilation by Kelley, *U. S. Bureau of Mines Bulletin*, 350, 394.

[10] The heat capacity of silver nitrate was measured recently in this Laboratory by Smith, Brown and Pitzer [THIS JOURNAL, **59**, 1213 (1937)] and their measurements are combined with data summarized by Kelley[9] at higher temperatures.

[11] The heat capacity of nitric oxide is an empirical equation calculated to fit the data of Johnston and Chapman [*ibid.*, **55**, 153 (1933)] for the temperature range from 300 to 500°K.

[12] Giauque, THIS JOURNAL, **52**, 4808 (1930).

values of the function $\Delta(F^\circ - H^\circ_0)/T$ and values of the true ΔH°_0 corresponding to the several measured values of $\Delta F^\circ/T$. We thus have the following:

$$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g);\ \Delta H^\circ_0 = 13{,}421 \pm 53 \text{ cal. per mole};\ \Delta F^\circ_{298.1} = 3547 \pm 60 \text{ cal. per mole};\ \Delta H^\circ_{298.1} = 13{,}379 \pm 60 \text{ cal. per mole};\ \Delta S^\circ_{298.1} = 32.98 \text{ E. U. (Method III)} \quad (11)$$

The differences between the values of $\Delta F^\circ_{298.1}$ and $\Delta H^\circ_{298.1}$ as given by Methods II and III are partly differences in the averaging of the values of the empirical algebraic ΔH°_0 on the one hand and the true ΔH°_0 on the other, and partly to the use of an average empirical equation for the heat capacity of nitric oxide in Method II. Equation 9 (Method II) is to be used when algebraic equations are required.

Since the completion of this investigation a paper by M. Tzentnershver and T. Checinski[13] dealing with the decomposition of silver nitrite has appeared. These authors investigated the decomposition reaction by a dynamic method. In the temperature range in which equilibrium is established with sufficient rapidity and in which their dynamic method may then be expected to yield equilibrium measurements, their results confirm our own. The reverse or synthesis reaction was not investigated, and hence they failed to observe solid solution effects at the higher temperature.

Summary

The equilibrium between solid silver nitrite, silver and silver nitrate and gaseous nitric oxide has been measured. We have calculated values of the $\Delta(F^\circ - H^\circ_0)/T$ function from existing data and have calculated the standard free energy, heat content and entropy increases at 25° by 3 independent methods.

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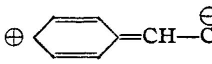
[13] M. Tzentnershver and T. Checinski, *Bull. intern. acad. polonaise sci. Classe sci. math. nat.*, **1935A**, 156 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

The Dipole Moments of Some Styrene Derivatives

BY H. L. GOEBEL AND H. H. WENZKE

It is a characteristic of unsaturated hydrocarbon groupings to attract electrons relatively to an alkyl group. Thus toluene has a moment of 0.4 with the negative end toward the benzene ring. In styrene two unsaturated groupings are linked together. The compound has a moment which experiment has shown to be opposite in direction to that of toluene.[1] In addition to the effect of induction the ethylenic grouping is in resonance with the benzene ring. Some of the more important forms of styrene are



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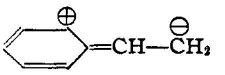
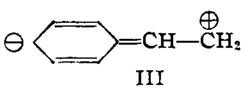
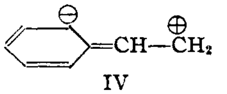


II



III

and



IV

The contributions of I and II are evidently greater than those of III and IV. The relative contributions of these forms are influenced by the replacement of one of the beta hydrogen atoms by other atoms or groups.

Preparation of Compounds.—The dioxane used as the solvent in these determinations was purchased from the Eastman Kodak Company. It was dried by refluxing with sodium and then distilled in all-glass Widmer distilling apparatus.

Cinnamic acid, methyl cinnamate, cinnamyl alcohol, cinnamyl chloride, γ-phenyl-*n*-propyl alcohol and γ-phenyl-*n*-propyl bromide also were purchased from the Eastman Kodak Company. These compounds according to their physical states at room temperature were either crystallized from suitable solvents or distilled through an efficient column so as to check melting points or boiling points reported in the literature.

Cinnamoyl amide was obtained by treating cinnamic anhydride with an ammonia solution according to a method reported by Autenrieth.[2] The amide was crystallized several times from hot water.

β-Cyanostyrene was prepared from cinnamoyl amide and phosphorus pentoxide in a manner similar to that proposed by Moureu and Lazennec[3] for preparing the corresponding acetylenic nitrile from the amide. The compound was crystallized repeatedly from a mixture of petroleum and diethyl ethers.

β-Nitrostyrene and *p*-methyl-β-nitrostyrene were prepared from nitromethane[4] and benzaldehyde and tolalde-

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[1] Otto and Wenzke THIS JOURNAL, **57**, 294 (1935).

[2] Autenrieth, *Ber.*, **34**, 186 (1901).

[3] Moureu and Lazennec, *Bull. soc. chim.*, **35**, 524 (1906).

[4] *Org. Syntheses*, **3**, 85 (1923).