



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<sub>2</sub> and B<sub>2</sub>, 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.

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

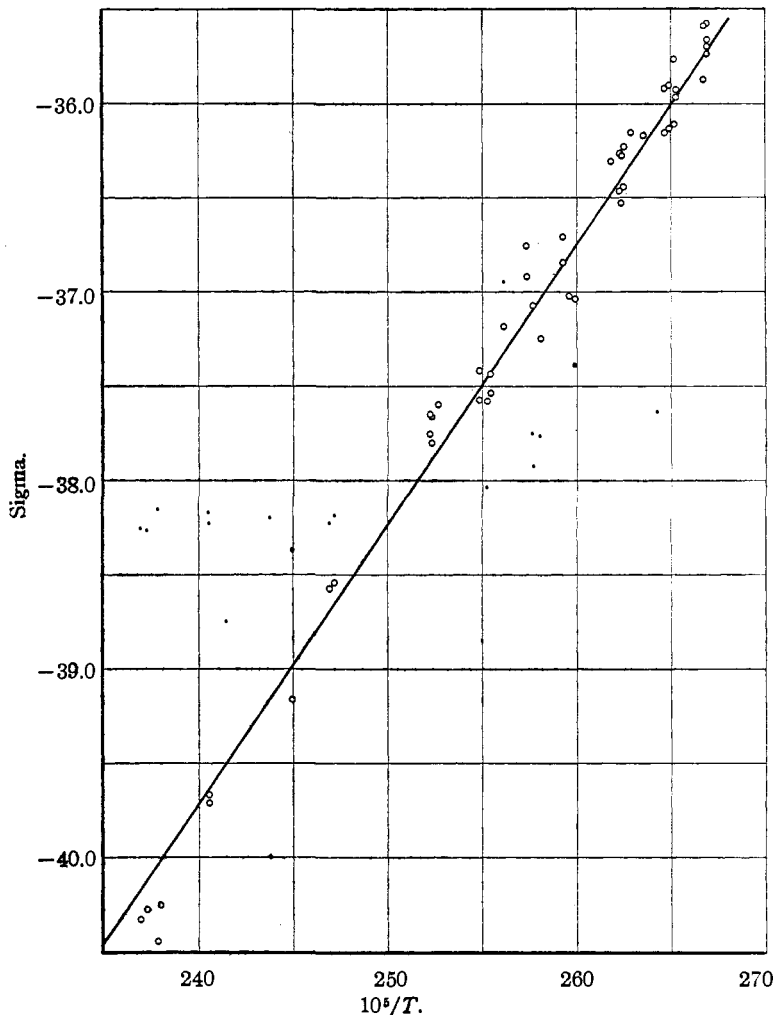


Fig. 2.— $2\text{AgNO}_3(\text{s}) = \text{Ag}(\text{s}) + \text{AgNO}_2(\text{s}) + \text{NO}(\text{g})$ .

Table I all the recorded values of  $-R \ln K$  which is equal to  $-4.575 \log P(\text{NO})$ . 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<sup>7</sup> we have plotted the value of sigma defined by the equation

$$\Sigma = \frac{\Delta H^\circ_0}{T} + I = -R \ln K - 6.95 \ln T + 0.00694T + 0.00000091T^2 \quad (2)$$

(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 <sub>2</sub> (s) = Ag(s) + AgNO <sub>3</sub> (s) + NO(g)					
	T	-R ln K		T	-R ln k
1A <sub>1</sub> +	388.6	1.848	34B <sub>2</sub> +	381.3	2.266
2B <sub>1</sub> -	388.6	1.682	35A <sub>2</sub> -	381.0	2.086
3A <sub>1</sub> +	392.4	1.072	36B <sub>2</sub> -	381.0	2.298
4B <sub>1</sub> +	392.4	1.226	37A <sub>2</sub> -	381.2	2.005
5A <sub>1</sub> -	391.5	1.100	38B <sub>2</sub> -	381.2	2.257
6B <sub>1</sub> +	391.5	1.197	39A <sub>2</sub> +	385.7	1.731
7A <sub>1</sub> +	415.7	-0.845	40B <sub>2</sub> +	385.7	1.867
9A <sub>1</sub> +	415.7	-0.821	41A <sub>2</sub> +	396.5	0.934
11A <sub>1</sub> +	421.5	-1.361	42B <sub>2</sub> +	396.5	1.037
13A <sub>1</sub> +	422.1	-1.410	43A <sub>2</sub> +	396.5	0.888
17A <sub>1</sub> +	420.5	-1.541	44B <sub>2</sub> -	396.4	1.028
19A <sub>2</sub> +	374.7	2.765	45A <sub>2</sub> +	405.0	0.198
20B <sub>2</sub> -	374.7	2.797	47A <sub>2</sub> -	404.6	.221
21A <sub>2</sub> -	374.7	2.724	50B <sub>2</sub> -	390.4	1.436
22B <sub>2</sub> -	374.7	2.884	51A <sub>2</sub> +	385.3	1.552
23A <sub>2</sub> -	374.9	2.584	52A <sub>2</sub> +	384.8	1.530
24B <sub>2</sub> +	374.9	2.873	54A <sub>2</sub> +	391.8	1.059
25A <sub>2</sub> +	377.0	2.518	56A <sub>2</sub> -	387.5	1.346
26B <sub>2</sub> +	377.0	2.555	58A <sub>2</sub> +	408.3	-0.360
27A <sub>2</sub> +	377.1	2.375	62A <sub>4</sub> +	388.1	1.529
28B <sub>2</sub> +	377.1	2.723	63A <sub>4</sub> -	379.4	2.341
29A <sub>2</sub> +	377.5	2.358	64A <sub>4</sub> +	395.8	1.086
30B <sub>2</sub> -	377.5	2.584	65A <sub>4</sub> -	382.0	2.233
31A <sub>2</sub> -	377.8	2.341	66A <sub>4</sub> -	380.4	2.367
32B <sub>2</sub> -	377.8	2.574	69A <sub>2</sub> +	420.3	-1.346
33A <sub>2</sub> +	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.

$$\text{AgNO}_2(\text{s});^8 S^{\circ}_{298.1} = 30.62 \text{ cal. per mole per deg.;} \\ C_p = 18.87 \quad (3)$$

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

$$\text{AgNO}_3(\text{s});^{10} S^{\circ}_{298.1} = 33.68 \text{ cal. per mole per deg.;} \\ C_p = 17.45 + 0.016T \quad (5)$$

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

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

$$\Delta F^{\circ}_T = 14,819 + 6.95 T \ln T - 0.00694 T^2 - \\ 0.0491 T^3 - 75.258 T \\ \Delta F^{\circ}_{298.1} = 3550 \text{ cal. per mole; } \Delta H^{\circ}_{298.1} = 13,412 \text{ cal.} \\ \text{per mole; } \Delta S^{\circ}_{298.1} = 33.083 \text{ E. U. (Method I) (7)}$$

(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<sup>9</sup> 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.

We might, perhaps, have chosen a slightly smaller value of  $\Delta H^{\circ}_0$  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  $\Delta H^{\circ}_0$  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<sup>7a</sup> (p. 453)

$$I = \Delta S^{\circ}_T + \Delta C_p (1 + \ln T) + \Delta C_p' T + \\ \frac{1}{2} \Delta C_p'' T^2 \quad (8)$$

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

$$\Delta F^{\circ}_T = 14,775 + 6.95 T \ln T - 0.00694 T^2 - 0.0491 T^3 - \\ 75.147 T; \Delta F^{\circ}_{298.1} = 3537 \text{ cal. per mole; } \Delta H^{\circ}_{298.1} = \\ 13,368 \text{ cal. per mole; } \Delta S^{\circ}_{298.1} = 32.98 \text{ E. U. (Method II)} \\ (9)$$

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

**Method III.**—The method suggested by Giauque,<sup>12</sup> 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

$$\frac{F^{\circ} - H^{\circ}_0}{T} = \frac{H^{\circ}}{T} - \frac{H^{\circ}_0 - S^{\circ}}{T} = \\ \frac{1}{T} \int_0^T C_p dT - \int_0^T C_p d \ln T \quad (10)$$

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<sup>11</sup> were used. The values at several round temperatures and for  $\Delta(F^{\circ} - H^{\circ}_0)/T$  are given in Table II.

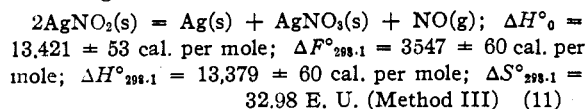
TABLE II

T, °K.	VALUES OF THE FUNCTION $(F^{\circ} - H^{\circ}_0)/T$				
	Ag(s)	AgNO <sub>2</sub> (s)	AgNO <sub>3</sub> (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

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

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



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  $\Delta H^\circ_0$  on the one hand and the true  $\Delta H^\circ_0$  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<sup>13</sup>

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

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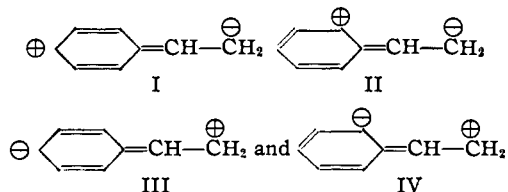
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

## 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.<sup>1</sup> 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



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.

(1) Otto and Wenzke *This Journal*, **57**, 294 (1935).

**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,  $\gamma$ -phenyl-*n*-propyl alcohol and  $\gamma$ -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.<sup>2</sup> The amide was crystallized several times from hot water.

$\beta$ -Cyanostyrene was prepared from cinnamoyl amide and phosphorus pentoxide in a manner similar to that proposed by Moureu and Lazennec<sup>3</sup> for preparing the corresponding acetylenic nitrile from the amide. The compound was crystallized repeatedly from a mixture of petroleum and diethyl ethers.

$\beta$ -Nitrostyrene and *p*-methyl- $\beta$ -nitrostyrene were prepared from nitromethane<sup>4</sup> and benzaldehyde and tolaldehyde.

(2) Autenrieth, *Ber.*, **24**, 186 (1901).

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

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