



# The Energy and Entropy of Activation of the Reaction Between Nitric Oxide and Chlorine

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# The Energy and Entropy of Activation of the Reaction Between Nitric Oxide and Chlorine<sup>1</sup>

IRVING WELINSKY AND H. AUSTIN TAYLOR New York University, New York City (Received April 23, 1938)

Following a discussion of the concept of entropy of activation and methods for its calculation, it is shown that the energy of activation of the formation of nitrosyl chloride from nitric oxide and chlorine is temperature dependent and permits an evaluation of the entropy of activation. A critical analysis is made of previous work.

**`HE** concept of entropy of activation was first introduced by Kohnstamm,<sup>2</sup> Scheffer<sup>3</sup> and Brandsma,4 but it was not given due consideration until La Mer<sup>5</sup> pointed out the necessity for its consideration in interpreting reaction kinetics, especially in solution.

Consider the reaction

$$A + B = C + D.$$

The velocities of the forward and reverse reactions,  $V_1$  and  $V_2$  are given in terms of concentrations by

$$V_1 = k_1 C_A C_B;$$
  $V_2 = k_2 C_C C_D,$ 

where  $k_1$  and  $k_2$  are the velocity constants of the forward and reverse reactions. At equilibrium,

$$V_1 = V_2 \quad \text{and} \quad F_1 = F_2,$$

where  $F_1$  and  $F_2$  are the free energies of reactants and resultants respectively. At any other point in the reaction, either  $V_1 > V_2$  when  $F_1 > F_2$  or  $V_1 < V_2$  when  $F_1 < F_2$ . The analogous behavior of velocity and free energy is suggestive of a correlation. For the following discussion, free energy will be defined by

$$F = E - TS + RT = E - TS^{0} + RT + RT \ln C$$
  
=  $F^{0} + RT \ln C$ .

where E, S and T are energy, entropy and temperature, respectively;  $S^0$  is the entropy in calories per degree per mole in the standard

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state of one mole per cc,  $F^0$  is the corresponding free energy in the standard state and C is the concentration in moles per cc. The free energy of the reactants is then

$$F_1 = F_A + F_B = F_1^0 + RT \ln C_A C_B,$$

whence  $C_A C_B = \exp((F_1 - F_1^0)/RT)$ or, from above,

$$V_1 = k_1 \exp((F_1 - F_1^0) / RT = C_1' \exp(F_1 / RT))$$

and 
$$V_2 = k_2 \exp((F_2 - F_2^0))/RT = C_2' \exp F_2/RT$$
.

At equilibrium the velocities and free energies being equal, the constants  $C_1'$  and  $C_2'$  are also equal but are not necessarily universal constants, as is easily shown. Substitution for the free energy gives

$$V_1 = C_1' \exp((F_1^0/RT) \cdot C_A C_B),$$

whence  $k_1 = C_1' \exp(F_1^0/RT)$ .

If now  $C_1'$  were a universal constant, it would be possible by measuring  $k_1$  at various temperatures to determine absolute values of free energy. Since this is impossible,  $C_1$  must contain an energy and entropy magnitude such that one can determine only free energy differences. If this free energy magnitude be represented  $F_x$ and taken out of the constant  $C_1$  leaving a residual constant  $C_1''$ , whence

$$C_1' = C_1'' \exp\left(-F_x/RT\right),$$

the velocity may be expressed:

$$V_1 = C_1'' \exp(F_1 - F_x) / RT = C_1'' \exp(-\Delta F_1 / RT).$$

This equation is in agreement with the Arrhenius hypothesis if  $F_x$  be recognized as the free energy of the activated complex.

<sup>&</sup>lt;sup>1</sup>An abstract from a thesis presented in partial fulfill-<sup>2</sup>Kohnstamm and Scheffer, Verslag. Akad. Weten-schappen, Amsterdam 19, 878 (1911).

<sup>&</sup>lt;sup>3</sup> Scheffer and Brandsma, Rec. trav. chim. **45**, 522 (1926). <sup>4</sup> Brandsma, Rev. trav. chim. **47**, 94 (1928); **48**, 1205 (1929)

<sup>&</sup>lt;sup>5</sup> V. K. La Mer, J. Chem. Phys. 1, 289 (1933).

This leads to an interesting point. Comparison of the free energies of reactants and resultants is logically made in the standard state where for the complex X,

$$F_x = F_x^0 + RT \ln C_x,$$

 $F_x^0$  being a function of temperature and  $RT \ln C_x$ , a function of temperature and concentration. The velocity constant  $k_1$  thus becomes from above:

$$k_{1} = C_{1}' \exp(F_{1}^{0}/RT)$$
  
or 
$$\ln k_{1} = F_{1}^{0}/RT + \ln C_{1}'$$
$$= (F_{1}^{0} - F_{x})/RT + \ln C_{1}''$$
$$= (F_{1}^{0} - F_{x}^{0})/RT + \ln C_{1}'' - \ln C_{x}$$
$$= (F_{1}^{0} - F_{x}^{0})/RT + \ln C_{1}$$
$$= -\Delta F_{1}^{0}/RT + \ln C_{1}$$
$$= -\Delta E_{1}/RT + \Delta S_{1}^{0}/R + \ln C_{1},$$

where  $C_1$  includes the concentration of the complex X and the universal constant  $C_1''$ :

$$C_1 = C_1^{\prime\prime} / C_x.$$

Similarly for the velocity constant of the reverse reaction:

$$\ln k_2 = -\Delta E_2/RT + \Delta S_2^0/R + \ln C_2,$$

 $C_2 = C_2^{\prime\prime} / C_x.$ where

 $C_1''$  and  $C_2''$  are universal constants and therefore equal. If  $C_1$  and  $C_2$  are to be equal, then  $C_x$ must be a constant for both the forward and reverse reaction. It must therefore be the equilibrium concentration of the intermediate complex.

This is as far as thermodynamics will go in the interpretation of reaction kinetics. The exact nature of the universal constant,  $C_1$  must be determined empirically or by some hypothetical mechanism. Posthumus,6 Rodebush7 and La Mer<sup>8</sup> have attempted to apply collision theory, but are unable to obtain the temperature dependent universal frequency which not only relates the specific rates of reversible reactions, but also serves as a quantity common to all reactions. This is reflected in La Mer's inability to separate the entropy term from the frequency of collisions; an inability to calculate entropies solely from the temperature dependence of the energy of activation, since it is only when the standard states are considered that one obtains a true entropy term and the universal frequency.

The activated complex theory of Eyring<sup>9</sup> appears to provide the simplest approach to this universal frequency, wherein the rate of reaction is controlled by the frequency of passage of activated complex molecules over a potential barrier. If the equilibrium constant, K, between reactants and activated complex be expressed in the conventional units and the frequency of passage over the barrier be expressed as the number of complexes in a length  $h/(2\pi m_x kT)^{\frac{1}{2}}$ rather than one centimeter of the barrier, the universal frequency is kT/h where, k, is the Boltzmann gas constant, h, is Planck's constant and, T, the absolute temperature. Then

$$RT \ln K \ddagger = -\Delta F^0 = -\Delta E + T \Delta S^0,$$

whence  $\ln k_1 = \ln kT/h - \Delta E/RT + \Delta S^0/R$ .

From this equation and a knowledge of velocity constants over a sufficiently wide temperature range, entropies may be calculated.

The applicability of the Arrhenius equation, with its inherent assumption of a constant energy of activation, indicates that for most reactions the temperature range over which the reaction may be conveniently followed is too small, although Kassel<sup>10</sup> has drawn attention to Bodenstein's<sup>11</sup> actual findings in the hydrogen iodide decomposition where the energy of activation increases at the rate of about 35 cal./degree. It was thought that the formation of nitrosyl chloride with its small temperature coefficient would permit reaction velocity determinations over a very extended temperature range. However, precisely because of the increasing temperature coefficient, with increasing temperature an upper limit of 300°C was set by the experimental arrangement used.

The reaction has already been studied very extensively<sup>12</sup> but with little consistency among

<sup>&</sup>lt;sup>6</sup> K. Posthumus, Rec. trav. chim. 52, 241 (1933).

<sup>&</sup>lt;sup>7</sup> W. H. Rodebush, J. Chem. Phys. 1, 440 (1933); 4, 744 (1936). <sup>8</sup> V. K. La Mer, reference 5. Also J. Am. Chem. Soc.

<sup>57, 2662, 2674 (1935).</sup> 

<sup>&</sup>lt;sup>9</sup> H. Eyring, J. Chem. Phys. 3, 107 (1935) et. seq.
<sup>10</sup> L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*, A. C. S. Monographs No. 57 (1932), p. 151.
<sup>11</sup> M. Bodenstein, Zeits. f. physik. Chemie 29, 295 (1898).
<sup>12</sup> Kiss, Rec. trav. chim. 42, 112 (1923); M. Trautz, Zeits. f. anorg. allgem. Chemie 88, 285 (1914); Trautz and Wachenheim, ibid. 97, 241 (1916); Trautz and Heng-

the results of various workers, for reasons which will be discussed later. The position of equilibrium is well known from the work of Trautz and Wachenheim<sup>13</sup> and of Dixon.<sup>14</sup> By studying both the decomposition and the formation of nitrosyl chloride, correlating the two by means of the equilibrium data, it has been possible to cover the temperature range from  $-25^{\circ}$ C to 300°C.

#### EXPERIMENTAL

#### Formation of nitrosyl chloride

Since the reactions involve a volume change the rates can be followed manometrically. A Bodenstein quartz spiral was used as a null instrument for this purpose, being sensitive to a pressure difference of 0.01 mm mercury. The reaction vessel, also of quartz, was connected to the NO and Cl<sub>2</sub> reservoirs through glass bellows valves of the Bodenstein type using fused silver chloride seats. The gases were therefore never in contact with mercury or grease and could not become contaminated. Chlorine was obtained pure by fractional distillation of tank chlorine. The nitric oxide was obtained by the action of mercury on lead chamber crystals in concentrated sulphuric acid. For the higher temperature a nichrome resistance furnace was used, temperatures being measured with a platinum resistance thermometer. For the lower temperatures, a concentrated aqueous calcium chloride solution cooled with powdered solid carbon dioxide, was used in a large bath. In all cases the temperature was constant to within  $\pm 0.3^{\circ}$ .

The rate of reaction is given by

 $2NO+Cl_2 = 2NOCl_1$  $d(\text{NOCl})/dt = k_3(\text{NO})^2(\text{Cl}_2) - k_2(\text{NOCl})^2$ 

where  $k_2$  and  $k_3$  are the velocity constants of the bimolecular reverse reaction and third order forward reaction. The equation was used in the approximate form:

 $\Delta(\text{NOCl})/\Delta t = k_3(\text{NO}_{AV})^2(\text{Cl}_{2AV}) - k_2(\text{NOCl}_{AV})^2,$ 

the constants being related with the equilibrium

constant as follows:

$$k_3/k_2 = (\text{NOCl})^2/(\text{NO})^2(\text{Cl}_2) = K$$

whence

$$k_{3} = \frac{K\Delta(\text{NOCl})}{\Delta t [K(\text{NO}_{AV})^{2}(\text{Cl}_{2AV}) - (\text{NOCl}_{AV})^{2}]}$$

The observed pressures were converted directly into concentrations in moles per cc using the ideal gas law. Total concentration was plotted against time and the initial concentrations were obtained by extrapolation to zero time. It should be noted that the chlorine was usually the first gas admitted into the reaction vessel. The initial partial pressure of this is therefore accurately known. The initial partial pressure of the second gas admitted was obtained from the extrapolation. The average values in the above equation were taken as the arithmetic mean of the concentration at the beginning and end of the time interval  $\Delta t$ , calculated from the smoothed curve of the total concentration-time plot. Table I presents the complete data for one experiment.

In Table II is presented a summary of the experiments performed.

It will be observed from Table I that  $k_3$  shows no trend throughout the experiment. In Table II the actual values of  $k_3$  differ from the mean by less than  $\pm 5$  percent. Variation of the relative concentrations of nitric oxide and chlorine has no effect on the value of the rate constant nor on the constancy of the values in any one experiment. The reaction is truly third order. This is also borne out by the recent work of Krauss and Saracini, but is contrary to the conclusions of Trautz and his collaborators who attempted to prove that the mechanism of the reaction involved the molecule NOCl<sub>2</sub> as an intermediate by observing rising constants when excess of chlorine was used and falling constants with excess nitric oxide. A critical analysis of all their data shows the presence of a number of errors.\* In many cases no account was taken of the reverse reaction. In others, the constants were calculated from zero time to time, t, during the reaction, which puts an undue emphasis on the initial concentrations. In still others, there is an unjustifiable averaging of scanty data.

lein, ibid. 110, 237 (1920); Trautz and Schlueter, ibid. 136, 1 (1924); Krauss and Saracini, Zeits. f. physik. Chemie 178A, 245 (1937).

 <sup>&</sup>lt;sup>13</sup> M. Trautz and F. Wachenheim, reference 12.
 <sup>14</sup> J. K. Dixon, Zeits. f. physik Chemie, Bodenstein Festband, 679 (1931).

<sup>\*</sup> See original thesis, I. Welinsky, New York University, 1938.

OBSERVED		INTERPOLATED		
Time (sec.)	Total Press. (mm)	TIME	Total Conc. (mole/cc)	$k_3$ (CC <sup>2</sup> /MOLE <sup>2</sup> /SEC.)
60	185.1	0	9.010×10 <sup>-6</sup>	
105	183.8			$3.52 \times 10^7$
165	182.2	$2 \times 10^{2}$	8.686	
230	180.6		0.425	3.77
325	176.6	4	8.435	2.66
435	175.3	6	8 248	3.00
540	172.6		0.240	3 72
600	171.6	8	8.096	0.12
690	170.3			3.79
795	168.6	10	7.970	
945	166.8			3.77
1050	164.4	12	7.865	
1230	163.1		7 770	3.64
1515	102.8	14	1.118	2 70
1650	150.6	16	7 700	5.19
1915	158.1	10	1.100	3 74
2165	156.6	18	7.632	
- [				3.84
		20	7.570	
			Mean	$3.73 \times 10^7$
		1		

TABLE I.

TABLE II.

Темр. °С Cl<sub>2</sub> (MM) NO (MM)  $k_3$ k3 (MEAN) -25.073.3 138.7 0.430×107 0.404×107 50.5 -25.0144.0 .387 -10.079.7 140.8 .661 .632 -10.075.4 143.1 .603 0.0 67.9 120.2 1.004 0.0 101.3 100.1 .868 .897 0.0 101.2 104.3 .897 99.4 100.5 0.0 .883 22.0 52.8 158.5 1.60 101.8 1.58 21.5101.0 1.597 22.0 69.3 136.5 1.68 22.054.2106.5 1.53 27.543.5 82.5 1.70 1.70 60.0 99.7 116.3 3.37 3.55 61.0 60.1 127.7 3.73 100.0 73.8 69.8 7.87 8.35 100.0 75.7126.28.83 146.0 59.6 63.3 20.13 18.35 146.0 47.376.5 18.57 196.0 50.3 52.5 49.1 45.8196.0 39.2 67.5 42.6 203.0 69.2 65.2 45.3 45.3

The effects of these errors is shown in Table III, which presents some of the values calculated by Trautz and his co-workers and the values recalculated from their observed data in the manner described above.

It must be noted that the recalculated values in Table III are themselves good constants for each run and not the result of any extensive or unjustified averaging. The falling or rising trends of velocity constants claimed by Trautz as indicative of an intermediate reaction are to be found only in his own work and in that with Schlueter. The data by Trautz and Wachenheim and by Trautz and Henglein show no trends and none are claimed by them. That the trends claimed in his own work are in every case fictitious may be illustrated by some examples. Trautz's Table I as recalculated gives the following constants:

Trautz	z Table I.
281.7°K $P_{\rm Cl_2} = 51.4$	$P_{\rm NO} = 129.6 \rm{mm}$
Time (sec.)	k 3
600	$1.15 \times 10^{7}$
800	1.16
1000	1.15
1200	1.08
1400	1.04
1600	1.03
1800	1.10

Trautz's conclusion that excess NO gives falling constants is obviously not justified. Again, Trautz's Table 14 when recalculated is as follows:

	Trautz Tab	le 14.	
451.1°K	$P_{\rm Cl_2} = 76.1 {\rm mm}$	1	$P_{\rm NO} = 67.4  \rm mm$
Time (s	sec.)	$k_3$	
400	)	$2.99 \times 10^{8}$	3
600	)	3.20	
800	)	3.00	
1000	)	2.94	
1200	)	2.92	

Here chlorine is in excess and the values are still constant within the experimental error. Actually Trautz claims a falling constant from 3.65 at 270 sec. to 3.10 at 960 sec.

The newer data by Trautz and Schlueter, which are supposed definitely to substantiate the suspected trends claimed in the earlier work, are based upon measurements made when the reaction was more than half completed. Krauss and Saracini also point out the scantiness of these data and the impossibility of attempting to recalculate constants from them. Furthermore, the data of Trautz and Schlueter are not selfconsistent. For example, on page 22 three

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experiments are reported. Experiment 20a, with excess NO shows the falling constants. 20b, with excess Cl<sub>2</sub> shows also falling constants, whereas by their theory they should rise, and finally 20c with excess NO shows good constants, whereas they should fall. In other words, their constants merely deviate from a mean by their normal experimental error, which appears to have been rather large.

With the exception of the Schlueter data, therefore, the work of Trautz and his co-workers really indicates the reaction to be truly third order and the agreement obtained upon recalculation of the third order constants with those here found is mutual confirmation of the validity of both.

The manner in which the data of the various investigators agree when correctly calculated is shown in Fig. 1. The curve has been drawn through the authors' data. The points referred to as decomposition were calculated from the equilibrium constant and the observed rate of decomposition of nitrosyl chloride. The two points of Kiss are the results of two separate investigations carried out ten years apart. Their agreement is good and the work shows none of

Temp. °C	$k_3$	k3 (RECALC.)
146.2	21.35×107	16.51×10
146.2	23.55	17.70
168.5	31.15	29.40
178.0	36.50	30.10
0.0	1.100	.767
0.0	1.018	.854
0.0	1.002	.846
0.0	1.106	.810
18.0	1.906	1.37
161.1	20.4	22.45

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the apparent anomalies reported by Trautz. The values obtained by Krauss and Saracini are consistently high and it is difficult to account for the discrepancy. It must be noted, however, that their work does not show the good internal consistency that is shown in the present work. Their values fall on a very good straight line which would intersect the indirect values at 150°C. Such a break in the curve is not to be expected.



### Decomposition of nitrosyl chloride

The nitrosyl chloride was prepared by the action of pure NO<sub>2</sub> on moist potassium chloride and purified by repeated distillation at  $-45^{\circ}$ C, the first and last fractions being discarded in each case. The same reaction system already described was used; the nitrosyl chloride being connected to the reaction chamber through a greaseless glass bellows valve. The procedure was identical with that previously mentioned, the velocity constants of formation being calculated in the same stepwise manner. Save at the highest temperature (300°C) the extrapolation to zero time in order to obtain the initial pressure is easily made. At 300°C an approximate extrapolation was first made and the constants calculated therefrom. If the extrapolation was correct, the constants calculated showed neither rising nor falling trend. If such a trend was found, various possible extrapolations were tried until constancy was obtained. The fact that the constants so found agree for different experiments justifies the mode of calculation. Table IV contains the results obtained.

The agreement with the data of Waddington and Tolman<sup>15</sup> is good. Fig. 1 shows how well the formation and decomposition data agree.

#### Energy of activation

From the curvature shown in Fig. 1, it is obvious that the energy of activation is steadily increasing with temperature. Using the approxi-

<sup>&</sup>lt;sup>15</sup> Waddington and R. C. Tolman, J. Am. Chem. Soc. 57, 689 (1935).

Темр. ⁰С	Po mm	$k_2$ (cc/mole/sec.)	$k_3 = k_2 K$ (CC <sup>2</sup> /MOLE <sup>2</sup> /SEC.)
200.0	144.2	78.0	4.74×10 <sup>8</sup>
200.0	158.5	74.3	4.51
250.0	99.5	1109.0	11.72
250.0	78.2	973.0	10.30
250.0	43.6	1109.0	11.72
250.0	<b>40.4</b>	1102.0	11.65
300.0	21.9	10320.0	25.9
300.0	23.5	9170.0	23.0
300.0	20.0	10750.0	26.9

TABLE IV.

m	<b>T</b> 7
LABLE	- V .

TEMP. INTERVAL °C	$\Delta E$ (cal.)
-25- 0	3730
0-50	4000
50-100	4460
100-150	5360
150-200	6400
200-250	7880
250-300	9860

mate equation,

$$\frac{\Delta(\log k_3 - 1/2 \log T)}{\Delta(1/T)} = -\frac{\Delta E}{2.3R},$$

the values given in Table V were calculated. It is apparent that, even taking into account the variation of the collision frequency with temperature still leaves a value for the energy of activation which rises with increasing temperature. Kassel<sup>16</sup> has shown that collision theory cannot account for the observed rate of this reaction by a factor of 10<sup>6</sup> even at the highest temperature, and the discrepancy is even larger at lower temperatures, where the energy of activation is smaller. Gershinowitz and Eyring,17 using the data of Trautz and Kiss to give a value for  $E_0$ , the energy of activation at the absolute zero, of 4780 cal. per mole, proceed thence to calculate the velocities at various temperatures by Eyring's method. The calculated values are lower than the observed by a factor of seven or eight. It is significant that the data in Table III would give a value of 4100 cal. using the method they adopted.

TABLE VI.

Temp. Interval °C	$\Delta E$ (cal.)	$\Delta S^0$ (cal./degree)
· · · · · · · · · · · · · · · · · · ·	FORMATION	
-25- 0	3,970	-12.85
0- 50	4,240	-11.32
50-100	4,900	-9.17
100-150	5,650	-7.80
150-200	6,950	-4.99
200-250	8,420	-2.08
250300	10,300	1.33
	DECOMPOSITION	
150-200	22,700	-2.73
200-250	25,800	3.47
250-300	28,300	8.04

To calculate entropies of activation, the energies of activation are first calculated, not as for the collision theory, but from a direct plot of log  $k_3$  against 1/T, and then applied in the equation previously derived:

## $\ln k_3 = \ln kT/h - \Delta E/RT + \Delta S^0/R.$

Table VI lists the results so obtained for both the formation and decomposition of nitrosyl chloride. It is interesting to note that the energy of activation at the absolute zero obtained by extrapolation of the above data is approximately 3500 cal.

In conclusion a word may be said in reference to the recent suggestion of Bodenstein<sup>18</sup> concerning a mechanism for the reactions of nitric oxide with oxygen, chlorine and bromine involving as a primary step the formation of a dimer (NO)<sub>2</sub> in every case. Assuming a heat of dimerization of 4000 cal., he has accounted for the decreasing rate of the  $NO-O_2$  reaction and the slowly increasing rates of the other two reactions with increasing temperature. It is well known that for the  $NO-O_2$  reaction the plot of log  $k_3$  against 1/T is noticeably curved at the higher temperatures. On Bodenstein's mechanism this could be accounted for by a varying heat of dimerization with varying temperature depending on the relative heat capacities of the monomer and dimer of NO. It is significant that the results here found for nitric oxide and chlorine show a more marked change in curvature at higher, than at lower temperatures and that the more marked curvature appears to set in at

<sup>&</sup>lt;sup>16</sup> L. S. Kassel, J. Phys. Chem. 34, 1777 (1930).

<sup>&</sup>lt;sup>17</sup> Gershinowitz and Éyring, J. Am. Chem. Soc. **57**, 985 (1935).

<sup>&</sup>lt;sup>18</sup> M. Bodenstein, Helv. chim. Acta. 28, 743 (1935); Zeits. f. physik. Chemie A175, 294 (1936).

approximately the same temperature range for both reactions. This would appear to constitute a further argument in favor of Bodenstein's mechanism.

The data for the entropy of activation given in Table VI covering the temperature range 150–300°C, the range covered by direct measurement of both the formation and decomposition, give by graphical interpolation a value of 6.1 for the entropy change of the reaction at 250°C. This may be compared with the value of 6.28 obtained by calculation from the entropies of nitric oxide,<sup>19</sup> chlorine<sup>20</sup> and nitrosyl chloride.<sup>21</sup> The agreement is very satisfactory.

 <sup>19</sup> H. L. Johnston and A. T. Chapman, J. Am. Chem. Soc. 55, 153 (1933).
 <sup>20</sup> W. F. Giauque and R. Overstreet, J. Am. Chem. Soc.

<sup>20</sup> W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

<sup>21</sup> F. P. Jahn, J. Chem. Phys. 6, 335 (1938).

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#### JOURNAL OF CHEMICAL PHYSICS

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# The Solid-Liquid Equilibrium in Argon

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University of North Carolina, Chapel Hill, North Carolina (Received June 10, 1938)

The method of investigating the equilibrium between solid and liquid phases, outlined in a previous paper, has been applied to argon. (In this method the intersections of the curves for the thermodynamic quantities  $T(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T + P$ , plotted as functions of the volume, are used to determine the conditions of equilibrium of the system.) Curves are found for the functions  $(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T$ , assumed dependent on volume and independent of temperature, which can reproduce with reasonable accuracy most of the melting parameters of argon at high pressures. The significance of these curves is discussed.

A S a preliminary to a theoretical study of the solid-liquid equilibrium, it seems desirable to make as complete an analysis as possible of the available experimental material for a substance in which the factors determining this equilibrium are as simple as possible. Argon seems to be a suitable substance for such a study, since the data available are fairly extensive, and since the intermolecular forces are of the pure van der Waals type.

The method we use is that presented in a previous paper,<sup>1</sup> and is based upon the thermodynamic equation

$$T(\partial S/\partial V)_T = (\partial E/\partial V)_T + P.$$
(1)

If the quantities  $T(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T + P$ are plotted as functions of the volume, the points of intersection of these curves determine the volumes of phases which are in internal equilibrium at the given temperature and pressure. Such an equilibrium is a stable rather than an unstable one (i.e., corresponds to a minimum

<sup>1</sup> Rice, J. Chem. Phys. 5, 492 (1937).

rather than a maximum of free energy) if  $(\partial E/\partial V)_T + P$  is greater than  $T(\partial S/\partial V)_T$  for values of the volume greater than the equilibrium volume. Of course, if there are two or more stable equilibria indicated in this way, in general one of them is the most stable; the condition that two phases be equally stable, and hence capable of coexistence, is that the area under the  $(\partial E/\partial V)_T + P$  curve between the volumes corresponding to the two phases should be equal to the similar area under the  $T(\partial S/\partial V)_T$  curve.

If the functions  $(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T$ changed very greatly with the temperature, such a method of analysis would be of little assistance. However, it seems probable that  $(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T$  can be considered, as a first approximation, as functions of the volume which are independent of the temperature, provided the temperature is sufficiently high so that quantization is not important. Inasmuch as the Debye characteristic temperature for argon is approximately equal to its normal melting point, it

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