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Citation: *The Journal of Chemical Physics* **10**, 646 (1942); doi: 10.1063/1.1723633

View online: <http://dx.doi.org/10.1063/1.1723633>

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## The Temperature Dependence of Reaction Rates from the Standpoint of the Broensted-Christiansen-Scatchard Equation

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(Received June 18, 1942)

In Section I arguments were presented for the necessity of splitting the  $\log k_{\infty}^*$  term in the general kinetic equation into a part which represents the rate constant extrapolated to a standard reference state of temperature, dielectric constant and concentration, and into a part giving the temperature dependence. In Section II the repulsive potential between reactants at close distances was formulated and this potential was then incorporated in the general kinetic equation to give the temperature dependence of the reaction rate constant. In Section III this equation was applied to existing kinetic data and found satisfactory. Also the repulsive forces between reactants calculated from the temperature and dielectric dependence of the reaction rate constants were compared with the intermolecular forces between the molecules of noble gases calculated from the second virial coefficients as evaluated by Fowler.

### I. INTRODUCTION

L AIDLER and Eyring<sup>1</sup> point out that a term of the form  $\phi/kT$  should be included in the kinetic equation to account for the non-electrostatic effects, which can be treated as repulsions beginning suddenly at the distance of closest approach, modified to take into account van der Waals attractions which may be of considerable importance. A similar term must account for the temperature dependence of the rate in the general kinetic equation<sup>2-4</sup>

$$\log k^* = \log k_{\infty}^* - z_A z_B e^2 / (DkT(r_A + r_B)) + z_A z_B e^2 \kappa / (DkT(1 + a\kappa)). \quad (1)$$

In this equation  $\ln k_{\infty}^*$  must be composite containing a term which represents the rate constant extrapolated to a standard reference state of temperature, dielectric constant and concentration, and a term giving the temperature dependence. Although it is generally recognized that the temperature and dielectric constant dependences of reaction rates are quite different, yet Eq. (1) as stated does not indicate this difference. The contrast between these two dependences can be shown as follows: If a reaction between ions is studied as a function of

the dielectric constant of the solvent at constant temperature, then from the slope of the curve obtained by plotting  $\log k_{\infty}^*$  versus  $1/D$ ,  $r_A + r_B$  can be obtained, provided that the effect of the solvent is that due to its dielectric constant, i.e., that predicted by electrostatic theory. The values of  $r_A + r_B$  obtained in these cases are always reasonable in magnitude and positive in sign. This is true because the slopes of the  $\log k_{\infty}^*$  versus  $1/D$  curves are of the right order of magnitude and of the right sign, i.e., the slopes are negative for ions of like charge sign and positive for ions of unlike charge sign.<sup>5,6</sup> If Eq. (1) were complete, one should be able, by using it, to obtain  $r_A + r_B$  from the slopes of plots of  $\log k$  versus  $1/T$ . However, irrespective of the signs of the charges on the reactants, the slopes of such plots are always negative as predicted by the Arrhenius equation, so that, for reactants of unlike charge sign  $r_A + r_B$  would be negative. The magnitude of  $r_A + r_B$  calculated from a temperature dependence will be roughly one-third to one-fourth that obtained from a dielectric constant dependence for ions of like charge sign, but in this case the sign is positive.

From these considerations, it follows that the  $\log k_{\infty}^*$  term must be composite and must embody a non-electrostatic potential which is predominant in determining the dependence of

<sup>1</sup> K. J. Laidler and H. Eyring, *Ann. New York Acad. Sci.* **39**, 303 (1940).

<sup>2</sup> J. N. Brönsted, *Zeits. f. physik. Chemie* **102**, 169 (1922); **115**, 337 (1925).

<sup>3</sup> J. A. Christiansen, *Zeits. f. physik. Chemie* **113**, 35 (1924).

<sup>4</sup> G. Scatchard, *J. Am. Chem. Soc.* **52**, 52 (1930); *Chem. Rev.* **10**, 229 (1932).

<sup>5</sup> E. S. Amis and V. K. LaMer, *J. Am. Chem. Soc.* **61**, 901 (1939).

<sup>6</sup> W. J. Svirbely and A. Schramm, *J. Am. Chem. Soc.* **60**, 330 (1938).

the rate upon the temperature. The purpose of this paper is the evaluation of this non-electrostatic potential together with a comparison of its magnitude with the value of electrostatic potentials with which we are more familiar.

## II. THE KINETIC EQUATION

It follows from the arguments which have been presented above that the mutual potential energy between two reacting particles cannot be restricted to their electrostatic potential energy. In order to obtain the observed temperature dependence of the rate constant a potential must be added which will correspond to the strong repulsive forces that exist for a close approach of the molecules, whether these are charged or not.

Following the line of thought introduced by Brönsted we shall assume that the reaction between two molecules *A* and *B* takes place via the formation of an intermediate complex *X*. Furthermore, we assume that spherical symmetry about each particle exists and that the mutual potential of two molecules *A* and *B*, if they are at the distance *r*, is given by an expression of the form

$$\psi(r) = \varphi_1(r) + \varphi_2(r). \quad (2)$$

Here  $\varphi_2(r)$  represents the contribution of the electrostatic forces in the case that *A* and *B* are charged (valency  $z_A$  and  $z_B$ , respectively). Thus, under the usual assumptions, we will have

$$\varphi_2(r) = \epsilon^2 z_A z_B e^{\kappa(a-r)} / (Dr(1+\kappa a)), \quad (3)$$

where  $\kappa$  is the parameter of Hückel and Debye's theory and *a* the distance of closest approach.

As to the origin and form of the potential  $\varphi_1(r)$  nothing need be assumed for our present purpose, except the following two conditions:

1. that  $\varphi_1$  is independent of the dielectric constant *D*, and
2. that  $\varphi_1$  has a positive value for those distances *r* at which formation of *X* occurs.

We shall call  $\varphi_1(r)$  the non-electrostatic potential though it may be traceable, in ultimate analysis, to forces of electric origin. However, in the latter case, it would have to be assumed that they are independent of the dielectric constant. There is

no contradiction in this assumption since, for the short distances involved, the notion of the dielectric constant (of the medium) loses its significance.

With the potential (2) and the concentrations  $C_A$ ,  $C_B$ , the probability of finding a molecule *B* at a distance between  $r_0$  and  $r_0 + dr_0$  from a molecule *A* will become proportional to

$$C_A C_B \exp(-\psi(r_0)/kT) r_0^2 dr_0. \quad (4)$$

Adopting as the criterion for the formation of *X* the fact that *r* should be within these limits the rate of reaction becomes<sup>3,4</sup> (with  $k^*$  and *K* constants):

$$k^* = KT^{1/2} (C_A C_B / C_x) \exp(-\psi(r_0)/kT). \quad (5)$$

Let  $k_0^*$  be the rate constant for some standard temperature  $T_0$ , and let the unimportant term  $T^{1/2}$  be neglected in the usual way, then we obtain our final formula

$$\log k^* = \log k_0^* + \psi(r_0)/kT_0 - \varphi_1(r_0)/kT - \epsilon^2 z_A z_B \exp(\kappa(a-r_0)) / (DkT r_0(1+\kappa a)). \quad (6)$$

It does not seem necessary for the present purpose to reduce  $k_0$  to concentration zero, nor to a standard value of the dielectric constant.

From (6) we obtain, for the dependence on  $1/T$

$$a_T = \frac{d \log k^*}{d(1/T)} = -(1/k) [\varphi_1(r_0) + \epsilon^2 z_A z_B \exp(\kappa(a-r_0)) / (Dr_0(1+\kappa a))], \quad (7)$$

and for the dependence on  $1/D$

$$a_D = \frac{d \log k^*}{d(1/D)} = -\epsilon^2 z_A z_B \exp(\kappa(a-r_0)) / (kT r_0(1+\kappa a)). \quad (8)$$

An inspection of formula (7) will show that  $a_T$  will be negative, whatever the charges  $z_A$  and  $z_B$  are, if the non-electrostatic potential (at  $r=r_0$ ) is sufficiently large compared with the electrostatic potential.

In the case of reactions which conform to electrostatics in their dependence on  $1/D$  it should be possible, from (7) and (8) and from the knowledge of  $a_T$  and  $a_D$ , to derive as well the value of the electrostatic potential  $\epsilon^2 z_A z_B / Dr_0$  as

TABLE I. Tests on inequalities (9) and (10).

Reaction	Medium	$T$	$D$	$a_T$	$a_D$	$T/D$	$a_T/a_D$
A. Ions of like sign							
$S_2O_8^{--} + I^-$	MeOH-H <sub>2</sub> O	313.1	73.12	-10140	-624	4.27	16.24
$B\phi B^{--} + OH^-$	MeOH-H <sub>2</sub> O	298.1	71.42	-11000	-737	4.18	15.24
$B\phi B^{--} + OH^-$	EtOH-H <sub>2</sub> O	298.1	71.42	-11120	-921	4.18	12.08
B. Ions of unlike sign							
$NH_4^+ + CNO^-$	MeOH-H <sub>2</sub> O	323.1	63.5	-9370	260	5.09	-36.0
$NH_4^+ + CNO^-$	Glycol-H <sub>2</sub> O	323.1	63.5	-10140	184	5.09	-55.2

TABLE II. A comparison of the non-electrostatic potentials at a distance  $r=r_0$  with electrostatic potential between ions

Reaction	Medium	$T$	$D$	$\phi_2(r_0) \times 10^{+12}$	$\phi_1(r_0) \times 10^{+12}$	$\phi_1(r_0)/\phi_2(r_0)$
$NH_4^+ + CNO^-$	MeOH-H <sub>2</sub> O	323.1	63.4	1.83	1.29	7.0
$NH_4^+ + CNO^-$	Glycol-H <sub>2</sub> O	323.1	63.4	1.28	1.39	10.9
$S_2O_8^{--} + I^-$	MeOH-H <sub>2</sub> O	313.1	73.12	3.66	1.39	3.8
$B\phi B^{--} + OH^-$	EtOH-H <sub>2</sub> O	298.1	73.42	5.27	1.52	2.9
$B\phi B^{--} + OH^-$	MeOH-H <sub>2</sub> O	298.1	73.42	4.22	1.51	3.6

that of the non-electrostatic potential  $\phi_1(r_0)$  for the critical distance.

Furthermore, it is easy to derive from (7) and (8) the following two inequalities which connect measurable quantities only:

1. if  $A$  and  $B$  have charges of the same sign:

$$a_T/a_D > T/D; \quad (9)$$

2. if  $A$  and  $B$  have charges of opposed sign:

$$a_T/a_D < T/D. \quad (10)$$

### III. APPLICATIONS

The first application will be to test the inequalities (9) and (10). Inequality (9) can be tested by the data on the persulfate-iodide reaction in methyl-water media<sup>7</sup> and the brom phenol blue-hydroxide reaction in both ethyl alcohol-water and methyl alcohol-water media.<sup>8</sup> From Table I it can be seen that  $a_T/a_D$  is three to four times as large as  $T/D$ . The predictions of inequality (10) can be applied to data on the ammonium-cyanate reaction in both methyl alcohol-water<sup>6</sup> and glycol-water<sup>8</sup> media. It is evident that in these cases  $a_T/a_D$  is less than  $T/D$ , to the extent of the inversion of the sign of  $a_T/a_D$ .

In Table II, the potentials  $\phi_1(r_0)$  and  $\phi_2(r_0)$  as well as their ratios are recorded for different sign and valence types of reactants in different media. In all cases the rate dependence on  $1/T$  was linear as demanded by both the Arrhenius equation and by Eq. (7). For bivalent-univalent reaction types the value of the non-electrostatic potential,  $\phi_1(r_0)$ , is roughly three times as great as the value of the electrostatic potential,  $\phi_2(r_0)$ , while in the uni-univalent type  $\phi_1(r_0)$  is from seven to eleven times as great. The electrostatic potential would be expected to be larger for the higher valence types of reactants. The solvent seems to play a rather important part in the ratios of these potentials.

As has been shown above, values of  $a_T$  and  $a_D$  permit the calculation of  $\phi_1(r_0)$  and  $\phi_2(r_0)$  for reaction rates obeying electrostatics in their dielectric constant dependence. If, however,  $a_D$  is not known,  $\phi_1(r_0)$  may still be calculated from  $a_T$  by use of Eq. (7), provided that  $r_0$  is known from some other source or provided that the second term on the right of Eq. (7) is neglected as a first approximation. Using this latter method of calculation for reactions between ions and molecules, molecules and molecules, and reactants in the gaseous state, the temperature dependence of the rates should yield values of  $\phi_1(r_0)$  substantially like those for reactions between ions in solution, since this potential arises from repulsive forces between the reactants

<sup>7</sup> E. S. Amis and J. E. Potts, Jr., J. Am. Chem. Soc. **63**, 2883 (1941).

<sup>8</sup> J. Lander and W. J. Svirbely, J. Am. Chem. Soc. **60**, 1613 (1938).

TABLE III. A comparison of the non-electrostatic potential between reactants calculated from the rate dependence on temperature alone and calculated from the rate dependence on both temperature and dielectric constant.

Reaction	Temp.	Range of d.c.	Temp. °C	Value used in calculating column 7 of d.c.	$\phi_1(r_0)$ from rate dependence on $T$ $\times 10^{+12}$	$\phi_1(r_0)$ from rate dependence on $T$ and $D$ $\times 10^{+12}$	Media
$S_2O_8^{--} + I^-^a$	20-40	55.0-76.7	40	73.12	1.39	1.04	EtOH-H <sub>2</sub> O
$B\phi B^{--} + OH^-^b$	5-45	64.5-78.5	25	71.42	1.52	0.93	EtOH-H <sub>2</sub> O
$B\phi B^{--} + OH^-^b$	5-45	64.5-78.5	25	71.42	1.51	1.13	MeOH-H <sub>2</sub> O
$NH_4^+ + CNO^-^c$	30-60	40.0-63.5	50	63.5	1.39	1.70	Glycol-H <sub>2</sub> O
$NH_4^+ + CNO^-^d$	30-70	35.0-69.9	50	63.5	1.29	1.32	MeOH-H <sub>2</sub> O
$B\phi BOH^- + H_3O^+^e$	25-45				2.12		EtOH-H <sub>2</sub> O
Sucrose + $H_3O^+^f$	21-41				1.83		EtOH-H <sub>2</sub> O
Sucrose + $H_3O^+^f$	21-41				1.67		Dioxane-H <sub>2</sub> O
$N_2O_5^g$	25-65				1.73		CCl <sub>4</sub>
$*AsO_3^{---} + FeO_4^{---h}$	89-120				0.74		H <sub>2</sub> O
$*Fe^{+++} + Sn^{+++}$	0-25				1.50		H <sub>2</sub> O
$2N_2O^i$	565-852				4.13		Gaseous
$C_2H_5OCOCl^k$	150-195				1.99		Gaseous
$2HI^l$	283-508				3.09		Gaseous
$H_2 + I_2^l$	283-508				3.06		Gaseous
$H + H_2(P)^m$	10-100				0.49		Gaseous

<sup>a</sup> See reference 7.<sup>b</sup> See reference 5.<sup>c</sup> See reference 8.<sup>d</sup> See reference 6.<sup>e</sup> E. S. Amis and J. B. Price, presented to J. Am. Chem. Soc. for publication.<sup>f</sup> E. S. Amis and F. C. Holmes, J. Am. Chem. Soc. **63**, 2231 (1941).<sup>g</sup> F. Daniels and E. H. Johnson, J. Am. Chem. Soc. **43**, 53 (1921); see F. H. MacDougall, *Physical Chemistry* (The MacMillan Company, New York, 1936), p. 404.<sup>h</sup> P. T. Stroup and V. W. Meloche, J. Am. Chem. Soc. **53**, 3331 (1931).<sup>i</sup> W. F. Timofeev, G. E. Muchin, and W. G. Gurewitsch, Zeits. f. Physik, Chemie **115**, 161 (1925).<sup>j</sup> C. N. Hinshelwood and R. E. Burk, Proc. Roy. Soc. **A106**, 284 (1924).<sup>k</sup> A. R. Choppin, H. A. Frediani, and G. F. Kirby, Jr., J. Am. Chem. Soc. **61**, 3176 (1939).<sup>l</sup> M. Bodenstein, Zeits. f. physik. Chemie **29**, 295 (1899); see H. S. Taylor and H. A. Taylor, *Elementary Physical Chemistry* (D. van Nostrand Co., New York, 1937), p. 242.<sup>m</sup> K. H. Geib and P. Harteck, Zeits. f. physik. Chemie, Bodenstein-Festband, 849-62 (1931); see H. S. Taylor and H. A. Taylor, *Elementary Physical Chemistry* (D. van Nostrand Co., New York, 1937), p. 235.<sup>n</sup>  $k$  was not extrapolated to  $k_\mu = 0$  in these cases.

at very close distances where the influence of the charge and of the dielectric constant is no longer appreciable.

In Table III are recorded the values of  $\phi_1(r_0)$  calculated in the two ways mentioned above and neglecting the second term on the right of Eq. (7) in the second method of calculation. The ionic examples included in the first method of calculation are all the instances recorded in the literature where sufficient data is given for this purpose and where the prerequisite of obedience to electrostatic theory is met. It is observable from Table III that the values of  $\phi_1(r_0)$  calculated from the temperature dependence of the rate correspond closely to the values of this function calculated from the dependence of the rate on both the temperature and dielectric constant. Furthermore, the variation between the two values is that predicted by electrostatics, i.e.,  $\phi_1(r_0)$  calculated from  $a_T$  and  $a_D$  is less than that calculated from  $a_T$ , neglecting the electrostatic term, for ions of like sign, and

vice versa for ions of unlike sign. It is also evident that for all reactions, whether in solution or in the gaseous state, and irrespective of charge type, the values of  $\phi_1(r_0)$  do not vary by an order of magnitude and in many cases agree in absolute value. It might be mentioned that, in the regeneration by hydrochloric acid of brom phenol blue from the colorless carbinol,<sup>9</sup> even though the reaction did not obey the requirements of electrostatics in its dielectric constant dependence of the rate, yet calculation of  $\phi_1(r_0)$  from the rate dependence upon temperature yielded a value of the non-electrostatic potential which compared favorably with that for the fading reaction the kinetics of which met the requirements of electrostatic theory.

As to the magnitudes of the non-electrostatic potential at the distance of reaction, they are of the expected order. Compared with the electrostatic energies, they are three to ten times as large if reasonable values of  $r_0$  are used. Further-

<sup>9</sup> See Table III, reference  $\epsilon$ .

more, they can be compared roughly with values of the intermolecular energies as calculated from the second virial coefficient. Fowler<sup>10</sup> has evaluated the coefficients  $\lambda$  and  $\mu$  in the well-known expression

$$\varphi_1(r) = \lambda r^{-s} - \mu r^{-6} \quad (11)$$

for values of  $s$  ranging from 8 to 14 applying Eq. (11) to noble gases. Of the reactions given above that between the ammonium-ion-cyanate ion involves reactants which correspond reasonably well in molecular weight to argon. Using

<sup>10</sup> R. H. Fowler, *Statistical Mechanics*, second edition (Cambridge, 1936), p. 306.

then, Fowler's constants for argon we obtain for  $\varphi_1(r_0)$ , with  $r_0 = 2.5 \times 10^{-8}$  cm as determined from Eq. (1), values between  $1.1$  and  $3.1 \times 10^{-12}$  when  $s$  ranges from 8 to 14. Thus our value of  $1.7 \times 10^{-12}$  is of the same order of magnitude. The good agreement, however, must be considered as fortuitous, as Eq. (11) is very sensitive to a change in  $r$ . For this reason the other reactions studied above do not agree nearly as well with Fowler's values, since, for these reactions, Eq. (1) yields values of  $r_0$  between 1.2 and  $1.7 \times 10^{-8}$  cm which are evidently somewhat small if consideration is taken of the large molecular weights of the reactants.

OCTOBER, 1942

JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

## An X-Ray Investigation of the Structure of Lead Chromate\*

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(Received July 13, 1942)

An attempt to analyze the structure of lead chromate was undertaken, using the Weissenberg x-ray goniometer technique. Positions of the lead and chromium atoms were determined. Although the intensities were carefully corrected for absorption, accurate values of the oxygen parameters could not be determined from the data at hand. Further work is indicated. There is some discussion of the migration of ions in the photoblackening effect which lead chromate exhibits.

BRILL<sup>1</sup> and others<sup>2,3</sup> have established that lead chromate (crocoite) is monoclinic with cell dimensions  $a = 7.10\text{\AA}$ ,  $b = 7.40\text{\AA}$ ,  $c = 6.80\text{\AA}$ ,  $\beta = 102^\circ 27'$ . There are 4 molecules ( $\text{PbCrO}_4$ ) per cell. The probable space group is  $C_{2h}^5 - P2_1/n$ . These data do not permit lead chromate to be classified with any of the previously determined structures in the oxyacid group of substances,<sup>4</sup> so that a detailed x-ray investigation would seem to be of interest. In addition, a knowledge of the structure is important for an interpretation of

the photoblackening process which lead chromate exhibits.

Simple rotation and Weissenberg equi-inclination<sup>5</sup> x-ray photographs were taken about the  $c$  and  $b$  axes. The indexing of these photographs verified the lattice and space group previously established. Unfiltered copper radiation was used throughout. Intensities were visually estimated. To aid in putting the intensities on a numerical

TABLE I.

Distance vector	Projection	$u$ $v$ $w$ (fractions of cell translations)		
		$u$	$v$	$w$
$(2x \ 2y \ 2z)$	$c$ face	0.43	0.30	
	$b$ face	0.45		0.80
$(\frac{1}{2} \ \frac{1}{2} - 2y \ \frac{1}{2})$	$c$ face	$\frac{1}{2}$	0.20	
	$b$ face	$\frac{1}{2}$		$\frac{1}{2}$
$(\frac{1}{2} - 2x \ \frac{1}{2} \ \frac{1}{2} - 2z)$	$c$ face	0.07	$\frac{1}{2}$	
	$b$ face	0.05		0.70

\* Submitted to the faculty of Bryn Mawr College in partial fulfillment of the requirements for the degree of doctor of philosophy. Gratitude is expressed to Dr. A. L. Patterson for his guidance and direction of the investigation. A grant made to Bryn Mawr College by the Elizabeth Thompson Science Fund made possible the purchase of much of the apparatus used.

<sup>1</sup> R. Brill, *Zeits. f. Krist.* **77**, 506 (1931).

<sup>2</sup> Gossner and Musgnug, *Zeits. f. Krist.* **75**, 410 (1939).

<sup>3</sup> S. von Glöckner, *Zeits. f. Krist.* **101**, 1 (1939).

<sup>4</sup> See R. W. G. Wyckoff, *The Structure of Crystals* (Chemical Catalogue Company, New York, 1931), second edition, Chap. 16.

<sup>5</sup> M. J. Buerger, *Zeits. f. Krist.* **88**, 356 (1934).