distinguishable from those given by our polymerization hypothesis; whether any explanation based on intermolecular forces, but not assuming compound formation, will do this becomes doubtful when we remember (see Fig. 1) that ΔE becomes constant long before "infinite dilution" is reached.

It is not claimed, finally, that a *concentration* treatment of amalgams is generally preferable to a treatment in terms of *activities*. The latter quantities are always valuable since they stand, by definition, in simple relation to the free energies of the amalgams, and thus bridge the gap between the thermodynamic functions for an amalgam and its stoichiometric composition. But when amalgams become experimentally indistinguishable from ideal solutions in the manner of Fig. 1, then it seems desirable to try a concentration treatment also, in order to determine whether the deviations from ideality at the higher concentration cannot be quantitatively accounted for by assuming polymerization of the solute; for we may discover in this way what molecular species actually exist in these amalgams.

SCHENECTADY, N. Y. RECEIVED OCTOBER 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Energies and Entropies of Activation of the Reaction between Bromoacetate and Thiosulfate Ions[1]

BY VICTOR K. LA MER AND MILDRED E. KAMNER

In the theory of chemical kinetics there are two important quantities which determine the specific rate constant k, namely, the energy of activation E_{act}, defined through the differential form of the well-known Arrhenius equation

$$\mathrm{d}\log k/\mathrm{d}T = E_{\text{act}}/2.3RT^2 \qquad (1)$$

and the action constant $B = \log \alpha$ in the integrated form, namely

$$k = \alpha\, e^{-E_{\text{act}}/RT} \qquad (2)$$

$$\log k = B - E_{\text{act}}/2.3RT \qquad (3)$$

E_{act} represents the average energy of those molecules which react minus the average energy of all the molecules in the system, all quantities being defined per mole. La Mer[2] has shown as a consequence of this definition of E_{act}, due to Tolman, that

$$B = \log \alpha = \frac{1}{2.3R}\int_0^T \left(\frac{\partial E_{\text{act}}}{\partial T}\right)\frac{\mathrm{d}T}{T} + \text{constant} \qquad (4)$$

determines the frequency with which the activated molecules react. In the special case where E_{act} remains independent of T at all temperatures, the integration constant in (4) equals log Z^0. In the case of unimolecular reactions Z^0 is the frequency of breaking the reactive bond in the activated molecule, whereas in a true bimolecular reaction Z° equals the collision frequency at unit concentrations. The dimension of B is time^{-1}.

The first term of B represents the increase in entropy due to the temperature dependence of E_{act} for the process, inactive molecules $\longrightarrow$ active molecules, and hence has been called[2] the entropy of activation. Further experimental evidence for the temperature dependence of B and E_{act} for a zero type reaction will appear in another paper.[3]

The present paper will deal primarily with the temperature dependence of the kinetic salt effect in a reaction between ions of the same sign to ascertain in how far interionic attraction influences E_{act} and B. The bromoacetate-thiosulfate ion reaction $BrCH_2COO^- + S_2O_3^= \longrightarrow S_2O_3CH_2COO^= + Br^-$ was selected for the experimental study since it is almost unique among ionic reactions for the absence of side reactions and the high precision with which the velocity constant can be determined.[4]

Accordingly, the experiments were designed to test the behavior of E and B for (a) change of temperature at constant concentration of reactants; (b) change of ionic strength (Brönsted–Debye effect) for the same temperature interval; (c) the effect of substituting high valence cations like La^{+++} for the lower valence ions Ba^{++} and Na^+ at the same ionic strength, and (d) the influence of dielectric constant produced by the addition of non-electrolytes.[5]

The Limiting Law for E_{act} and B.—Equation

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[1] A preliminary report of these data was given in THIS JOURNAL, **55**, 1739 (1933). A more complete report was read at the St. Petersburg, Florida, meeting of the Society in March, 1934.

[2] La Mer, *J. Chem. Phys.*, **1**, 289 (1933); THIS JOURNAL, **55**, 1739 (1933).

[3] V. K. La Mer and M. L. Miller, *ibid.*, **57**, 2674 (1935).

[4] La Mer and Fessenden, *ibid.*, **54**, 2351 (1932).

[5] La Mer and Kamner, *ibid.*, **57**, 2669 (1935).

(1) and the Brönsted equation $\log k = \log k^0 + \log f_A f_B / f_X$ yields

$$\begin{aligned} E_{\text{act}} &= E^0_{\text{act}} + [\bar{L}_X - (\bar{L}_A + \bar{L}_B)] \qquad (5) \\ &= E^0_{\text{act}} + \Delta\bar{L}_{\text{act}} \end{aligned}$$

when we recall that $\bar{L} = -RT^2 \partial \ln f / \partial T$.

The superscript zero refers to the standard state of infinite dilution. $\bar{L} = H - H^0$ is the *relative* partial molal heat content, so that $\Delta\bar{L}_{\text{act}}$ may be called the heat of dilution for the activation process $A + B \rightleftarrows X$.

Similarly by using eq. (4), B can be decomposed into the components.

$$\begin{aligned} B &= B^0 + [\bar{S}_X - (\bar{S}_A + \bar{S}_B)] \qquad (6) \\ &= \log Z^0 + S^0_{\text{act}}/2.3R + \Delta\bar{S}_{\text{act}}/2.3R \end{aligned}$$

$\Delta\bar{S}/2.3R$ is the increase in entropy of activation arising from interionic attraction.

When the thermodynamic operators $\bar{S} = -\partial\bar{F}/\partial T$ and $\bar{H} = \partial(\bar{F}/T)/\partial(1/T)$ are applied to the Debye–Hückel limiting law

$$\begin{aligned} \bar{F}_i &= -N(\epsilon Z)^2\kappa/2D \qquad (7) \\ \kappa &= C(DTV)^{-1/2} \end{aligned}$$

one obtains on substituting Wyman's values[6] of $\partial \ln D/\partial \ln T = -1.371$ for water at 25°, that

$$\begin{aligned} \bar{L}_i &= \bar{F}_i \left[3/2 \frac{\partial \ln D}{\partial \ln T} + \frac{1}{2}\frac{\partial \ln V}{\partial \ln T} + 3/2\right] \qquad (8) \\ &= \bar{F}_i\,[-0.51] \end{aligned}$$

$$\begin{aligned} \bar{S}_i &= \bar{F}_i/T \left[3/2\, \partial \ln D/\partial \ln T + \frac{1}{2} \partial \ln V/\partial \ln T + \frac{1}{2}\right] \qquad (9) \\ &= \bar{F}_i/T[-1.52] \end{aligned}$$

It is important to emphasize that in the limit for high dilutions, the *reversible* heat of dilution $(-T\bar{S}_i)$ is almost exactly three times greater, *but opposite in sign* to the *irreversible* heat of dilution $(\bar{H}_i)$. Now

$$\bar{F}_i/2.3RT = \log f_i = -0.506 Z_i^2 \sqrt{\mu} \qquad (10)$$

and $Z_x^2 = (Z_A + Z_B)^2$, hence

$$\Delta\bar{L}_{\text{act}}/2.3RT = 0.51 Z_A Z_B \sqrt{\mu} \qquad (11)$$

$$\Delta\bar{S}_{\text{act}}/2.3R = 1.52\, Z_A Z_B \sqrt{\mu} \qquad (12)$$

The Brönsted–Debye equation, accordingly, can be written

$$\begin{aligned} \log k = {} & [\log Z^0 + S^0_{\text{act}}/2.3R + 1.52\, Z_A Z_B \sqrt{\mu}] \\ & - [E^0_{\text{act}}/2.3RT + 0.51 Z_A Z_B] \sqrt{\mu} \qquad (13) \end{aligned}$$

The limiting slope of the experimental quantities $\log k$, B, and $E_{\text{act}}/2.3RT$ when plotted against $Z_A Z_B \sqrt{\mu}$ should be, respectively, 1.01, 1.52 and 0.51. Equation (11) thus predicts that in the limit of high dilutions the energy barrier, E_{act}, should increase by 684 $Z_A Z_B \sqrt{\mu}$ calories/mole as a result of interionic attraction. On the prevailing view[7] that the function of a catalyst is to provide a lower by-pass in the energy barrier, one would be forced to conclude that the addition of a neutral salt should *decrease* the rate of a reaction between ions of the same sign—a conclusion which is contrary to abundant experimental evidence. The explanation is that the action constant B increases concomitantly in the limit about three times as rapidly as E_{act}, and hence B plays the predominant role in determining the magnitude of the neutral salt catalysis.

Preparation of Materials

Bromoacetic acid was redistilled at reduced pressure, sodium thiosulfate was recrystallized and solutions of sodium hydroxide and of potato starch were prepared as in earlier experiments.[8] Iodine was sublimed from a potassium iodide–iodine mixture, resublimed and stored over calcium chloride in a desiccator until used in the preparation of standard iodine solutions. The latter always contained 4% of Mallinckrodt neutral potassium iodide, Analytical Quality, the iodate content of which is not over three parts per million. Sodium chloride and barium chloride were recrystallized once and dried at a temperature exceeding 100°. Lanthanum chloride, precipitated from aqueous solution by hydrogen chloride, was washed with alcohol, air dried and stored over phosphorus pentoxide or calcium chloride. This sample yielded values for velocity constants which checked with those for solutions containing a Welsbach cerium-free lanthanum chloride purified several years earlier.[9]

Experimental Procedure

Two types of technique were employed for the bromoacetate–thiosulfate reactions.

1. For experiments in which the time error in starting and stopping the reaction is negligible, equal volumes of equimolar solutions of the reactants were mixed and the reaction was stopped by iodine titration as described by La Mer and Fessenden.[4]

2. A special type of flask, shown in Fig. 1, was devised to reduce errors in timing the more rapid reactions. The flasks were immersed in the thermostat, 50 cc. of sodium bromoacetate

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[6] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

[7] Getman-Daniels, "Outlines of Theoretical Chemistry," 5th Ed. John Wiley and Sons, Inc., New York City, 1931, p. 348.

[8] V. K. La Mer and M. E. Kamner, THIS JOURNAL, **53**, 2832 (1931).

[9] V. K. La Mer and R. G. Cook, *ibid.*, **51**, 2624 (1929).

solution was pipetted into (a) and 50 cc. of sodium thiosulfate solution of equal molarity was pipetted into (b). After temperature equilibrium had been reached the reaction was started by tipping the flask sidewise and prompt mixing was achieved by pouring the solution back and forth in the two compartments of the flask. To stop the reaction, iodine just insufficient to neutralize the remaining thiosulfate was pipetted into (a), then poured into (b) at a recorded time. The flask was placed in an ice-bath; the stopper and sides were washed down with about 50 cc. of cold distilled water; starch was added and the titration with iodine solution was completed as quickly as possible. The addition of 0.1 cc. of 0.1 *M* acetic acid to the solution before completion of the titration eliminated any possible error due to presence of hypoiodite. With this technique the error in starting and stopping the reaction was reduced to two to three seconds so that reactions involving times ranging from fifteen minutes to an hour yielded velocity constants as reproducible as those of slower reactions.

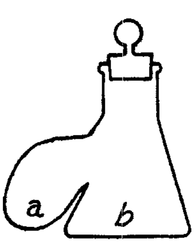

Fig. 1.

Corrections to be made to the end-point of iodine titrations were determined as the volume of the given iodine solution required to produce the same blue color in an equal volume of water containing starch and potassium iodide at the temperature of titration. The use of a daylight lamp improved the precision of the end-point in artificial light.

The fluctuations in the temperature of the thermostat rarely exceeded 0.01° during any of the experiments, except at 50° where the precision of the time average was ±0.01°. Any errors entering into the absolute temperatures, which were determined by the use of the ice-point and of a thermometer calibrated by the Bureau of Standards, cannot be of sufficient magnitude to make any significant difference in the data. For a temperature interval of 25° the uncertainty in E_{act} arising from the uncertainty in temperature is estimated as 0.16% and for a 12.5° interval 0.32%; that is, the order of 24 or 48 calories, respectively.

At 50° eight carefully conducted experiments (no added neutral salts) exhibited a small but reproducible decrease in the velocity constant with the progress of the reaction. The reaction is very rapid at 50° but the drift at this temperature does not appear to be due to errors in timing. We attribute the difficulty to intrusion of the spontaneous water reaction $H_2O + CH_2BrCOO^- \longrightarrow CH_2OHCOO^- + H^+ + Br^-$. This reaction is of entirely negligible velocity at 25 and 37.5° ($k_{25} = 2.8 \times 10^{-6}$) but assumes sufficient importance to vitiate highly precise results at 50°. No data or conclusions are submitted in this paper for temperatures higher than 37.5°.[10]

Recently, Kiss and Vass[11] have reported temperature coefficient data for this reaction over the range 5 to 55°.[12]

The results for the water reaction at 25 and 50° are recorded also in Table I. The method employed consisted in bringing the aqueous solution of sodium bromoacetate to temperature as quickly as possible. The hydrogen ion formed by the hydrolytic reaction was neutralized with sodium hydroxide to a *p*H of 7 at frequent intervals to prevent acid catalysis, using bromthymol blue as indicator. Minor sources of error are incomplete temperature equilibrium at the beginning of the reaction, and the influence of carbon dioxide upon the titration values. To increase the precision, a large number of measurements was made, and the early readings which were burdened with time and temperature errors discarded. The velocity constants for the progressive time intervals were compared with those calculated from the initial time. The $E_{(25-50)}$ for the bromoacetate–water reaction was reproducible to about 0.7% (175 cal.). For typical experiments illustrating the high precision and constancy of the individual velocity constants of the thiosulfate reaction, the reader is referred to the following paper.

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[10] A. N. Kappanna [*J. Indian Chem. Soc.*, **6**, 45 (1929)] reports velocity constants for the thiosulfate reaction at 30, 40 and 50° at eleven concentrations ranging from $\mu = 0.0025$ to 0.085. He states "The *temperature coefficient* of reaction velocity constant on either side of 40° and at different ionic strengths has *almost* the same value, within *narrow* limits 2.2 to 2.3 for a rise in temperature of 10° C." (Italics ours.) Our calculations of his data show that E_{30-40} is 15,320 ± 500 calories an average deviation from the mean which is about ten times as great as ours. *Cf.* Moelwyn-Hughes, "Kinetics of Reactions in Solutions," p. 201, for a similar calculation.

[11] Kiss and Vass, *Z. anorg. allgem. Chem.*, **217**, 305–320 (1934).

[12] They claim that log k varies linearly with $1/T$ in all cases. An examination of their Table 8, however, shows that their E_{act} values for 10-degree intervals fluctuate so irregularly and so violently with temperature (800 calories for the interval 5–15° and 15–25°) that one can only conclude that their experimental errors are too large to establish deviations from a temperature independent E_{act}. On the other hand, the data in their Tables 1 and 4 are sufficiently consistent to support our conclusion that the salt catalysis is primarily the result of an increase in the entropy of activation, and certainly does not result from any decrease in the energy of activation.

Calculations

The bimolecular velocity constants were calculated from the formula, $k = \frac{1}{t} \times \frac{1}{a} \times \frac{x}{(a-x)}$ applicable when $a = b$ = moles of reactants per liter of solution. The time, t, is expressed in minutes. All solutions were standardized at room temperature. However, the correct molarity to be substituted in the bimolecular equation at other temperatures differs slightly from the molarity at 25°, because of the expansion or contraction of the solution. To obtain k in moles per liter at the temperature of reaction, the velocity constant at $t°$ was multiplied by the factor

$$\frac{\text{(volume of 1 g. of water at } t°)}{\text{(volume of 1 g. of water at 25°)}}$$

The values of k used in calculation of the energy of activation are the values of k for the molarity at the temperature indicated. This introduces a very small further correction. $\Delta \log k$ must be obtained as the difference of the logarithms of two velocity constants at different temperatures but for identical volume-molar concentrations. Hence, a correction of $\left[\frac{d \log k}{d\sqrt{\mu}} (\sqrt{\mu_{t_0}} - \sqrt{\mu_{25}})\right]$ has been subtracted from $\log k_{\text{obsd.}}$ at $t°$. It does not exceed 0.0003.

Method of Calculating Precision of E Values

The error in average log k is estimated so as to take account not only of the error in the mean k in each of one or more experiments, but also the difference between two mean k values for two separate experiments, whenever these were performed. Thus, it is a measure of precision within a given experiment and of the reproducibility of the value. The error in Δ log k is evaluated as the square root of the sum of the squares of the errors in the two average log k values from which it is derived. An error of 25 calories in the determination of E produces an uncertainty of 0.02 units in B in eq. (3).[13]

Discussion of Results

Table I contains the data for log k for the bromoacetate-thiosulfate ion reaction for various temperatures and additions of neutral salts. These data are plotted in part in Fig. 2 for 0 and 25° to illustrate the specific character of the positive salt catalysis in the presence of Ba^{++} and La^{+++} ions, and the parallelism of the curves at the two temperatures in the absence of these high valence ions.

The values E_{act} are given in the next to the last column. They indicate that E(0–25°) increases by 127 ± 60 calories (15,881 to 16,008) on passing from $\sqrt{\mu} = 0.0895$ to 0.141, and decreases slowly to 15,941 calories at $\sqrt{\mu} = 0.447$. The initial rise in E_{act} appears to be greater than the demands of the limiting law but the probable experimental error is too large for the short interval to warrant a definite conclusion. An examination of the calorimetrically determined values of $\overline{H}$ for salts shows that the individual deviations[14] from the limiting law persist to much lower concentrations than is the case for the function $\overline{F}$. In fact $\overline{H}$ for sodium iodate, potassium nitrate and barium nitrate passes through a maximum in the neighborhood of $\sqrt{\mu} = 0.10$ quite similar to the behavior of E_{act}. The action constant B rises sharply from 11.19 ($\sqrt{\mu}$ = 0.0895) to 11.35 ($\sqrt{\mu} = 0.141$) at a rate which is slightly greater than the limiting law prediction. For further increases of μ, B rises less rapidly but steadily to 11.55 at $\sqrt{\mu} = 0.477$. See Figs. 3 and 4. It will be noted that in this case where the ionic strength increase results solely from an increase in concentration of the reactants in the form of their sodium salts, the increase in log k is due primarily to an increase in B and only secondarily if at all to a variation in E_{act}. In the following paper the rate of this reaction in

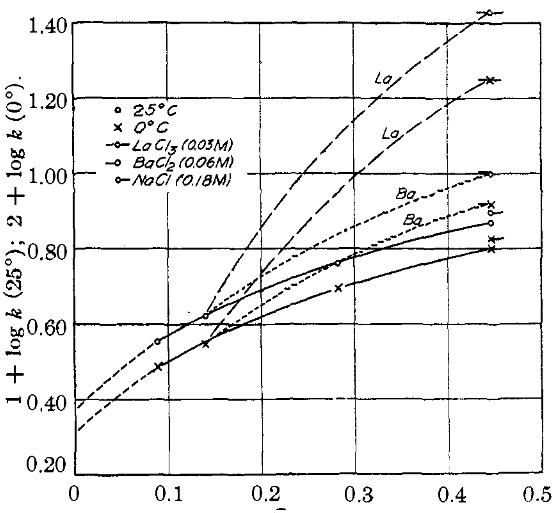

Fig. 2.

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(13) The correction to the energy of activation arising from the dependence of the collision number upon $\sqrt{T}$ amounts to −278 calories for the (0–12.5°) range and to −303 calories for the (25–37.5) range. This correction would magnify the decrease of E with T from 0 to 37.5° by 25 calories and thus strengthens slightly the conclusion that E_{act} is a function of T.

(14) Lange and Robinson, ref. 6, Figs. 8 and 10.

TABLE I

LOG *k*, *E* AND *B* DATA FOR THE REACTION SODIUM BROMOACETATE AND SODIUM THIOSULFATE IN AQUEOUS SOLUTION WITH AND WITHOUT ADDED NEUTRAL SALTS

Concn. moles/ liter	t,° C.	Detns.	Conversion range %	k Corrected to m/l at 25°	2 + log k	2 + av. log k corr.	Δ log k	E	B
Sodium Bromoacetate and Sodium Thiosulfate									
0.002	0	5	12–25	0.03084 ± 0.00007	0.48911 ± 0.001	0.49067	1.06491 ± 0.0018	15,881 ± 30	11.19
.002	0	2	29	.03109 ± .00005	.49262 ± .0007				
.002	25	5	22–68	.3594 ± .0012	1.55558 ± .0015	1.55558			
.005	0	4	39–58	.03523 ± .00003	0.54691 ± .0004	0.54669	0.56244 ± .0011	16,072 ± 30	11.41
.005	12.5	4	7–46	.1286 ± .0003	1.10924 ± .0010	1.10913		(16,008)	
.005	25	4	37–71	.4187 ± .0002	1.62190 ± .0002	1.62034	0.51121 ± .0016	15,946 ± 50	11.30
.005	25	6	40–74	.4162 ± .0006	1.61930 ± .0006	± .0013	0.46742 ± .0014	15,856 ± 50	11.24
.005	37.5	5	17–60	1.223 ± .0015	2.08743 ± .0005	0.08776			
.02	0	5	47–71	.04902 ± .00007	0.69037 ± .0006	2.68994	1.07176 ± .0007	15,983 ± 10	11.48
.02	25	4	52–59	.5777 ± .0002	1.7610 ± .0002	1.76170			
.05	0	5	18–50	.06344 ± .00029	0.80236 ± .0020	2.80203	1.06896 ± .0021	15,941 ± 30	11.55
.05	25	4	35–72	.743 ± .001	1.87099 ± .0006	1.87099			
Sodium Bromoacetate and Sodium Thiosulfate: 0.18 M in NaCl									
0.005	0	5	9–48	0.06675 ± .00007	0.82445 ± .0005	0.82423	0.56730 ± .0013	16,211 ± 40	11.79
.005	12.5	5	17–62	.2464 ± .0007	1.39164 ± .0012	1.39153		(15,947)	(11.59)
.005	25	4	13–53	.784 ± .005	1.89432 ± .0030	1.89432	.50279 ± .0032	15,683 ± 100	11.38
.005	37.5	3	27–49	2.233 ± .007	2.34889 ± .0014	2.34922	.45490 ± .0033	15,431 ± 120	11.19
( ) Values for 0–25°.									
Sodium Bromoacetate and Sodium Thiosulfate: 0.06 M in $BaCl_2$									
0.005	0	5	11–51	0.08212 ± 0.00005	0.91445 ± 0.0003	0.916	0.57225 ± .002	16,353 ± 60	12.00
.005	0	4	8–31	.08273 ± .00012	.91766 ± .0006	± .001		(16,248)	(11.92)
.005	12.5	5	25–69	.3086 ± .0005	1.48940 ± .0007	1.488			
.005	12.5	5	31–68	.3069 ± .0006	1.48700 ± .0009	± 0.001	.51730 ± .002	16,136 ± 60	11.83
.005	25	3	23–57	1.014 ± .003	2.00604 ± .0013	2.00530			
.005	25	4	23–60	1.011 ± .001	2.00475 ± .0004	± 0.0015			
.005	37.5	4	31–48	2.972 ± .009	2.47305 ± .0013	2.473	.46767 ± .002	15,864 ± 60	11.61
.005	37.5	4	31–61	2.968 ± .014	2.47246 ± .0020	± 0.002			
Sodium Bromoacetate and Sodium Thiosulfate: 0.03 M in $LaCl_3$									
0.005	0	4	18–49	0.117 ± 0.002	1.248 ± .005	1.245			
.005	0	5	15–54	.174 ± .001	1.241	± 0.005	0.611 ± .005	17,500 ± 150	13.3
.005	12.5	4	23–47	.7181 ± .0014	1.85618	1.85622		(17,780)	(13.46)
.005	12.5	4	24–64	.7182 ± .0007	1.85625	± 0.0004			
.005	25	4	30–66	2.724 ± .003	2.43521		0.57875 ± .0007	18,052 ± 25	13.66
.005	25	4	21–69	2.721 ± .009	2.43473	2.43497 ± 0.0005			
.005	37.5	10	32–68	8.8 ± 0.2		2.944 ± .010	0.509 ± 0.01	17,270 ± 350	13
Log k, E and B Data for the Reaction Sodium Bromoacetate and Water									
					6 + log k corr.				
0.05	25	7	10–45		0.4440 ± 0.003		1.4121 ± 0.004	24,915 ± 70	12.69
.05	50	10	18–74		1.8561 ± .0024				
.1	25	7	8–42		0.5276 ± .010		1.4013 ± 0.01	24,725 ± 175	12.64
.1	50	11	9–66		1.9289 ± .001				

the presence of 32.4% sucrose is reported. In this solvent we find that B increases from 11.02 to 11.49 or 0.47 units for the same range of concentration of reactants, while E_{act} rises slowly but at a lower level than for water.

The addition of 0.18 M sodium chloride to $a = b = 0.005\ M$ to produce $\sqrt{\mu} = 0.447$ yields E (0–25) = 15,947 and B(0–25) = 11.59. These values do not differ very significantly from those for $a = b = 0.05\ M$ ($\sqrt{\mu} = 0.447$) and we may conclude that chloride ions exercise no specific effect on either E or B.

On the other hand, the presence of 0.06 M barium chloride and particularly 0.03 M lanthanum chloride to produce the same $\sqrt{\mu} = 0.447$ produces a marked increase in both B and E. In the presence of 0.03 M lanthanum chloride E increases by 1780 cal and B increases from 11.55 to 13.46 or almost two logarithmic units.

The substitution of La^{+++} for Na^+ (and to a less degree Ba^{++} for Na^+) creates a situation in which the reactant anions must cluster about the La^{+++} ion. By referring to the Fig. 2 of La Mer and Fessenden, where log k (25°) is plotted against $\sqrt{\mu}$, it will be noted that log k increases rapidly for small additions of La^{+++} but reaches at low concentrations what appears to be a constant saturation value. This behavior can be explained qualitatively on the basis of the higher terms of the Gronwall-La Mer equation, or when $(Z_1Z_2\epsilon^2/DakT)$ becomes too large for rapid convergence, by the more pictorial but essentially equivalent concept of ion-association as defined by Bjerrum. Thus, the later theory predicts[15] that in the presence of La^{+++} most of the reactants will exist as ion-associated pairs of the type $(LaS_2O_3)^+$ colliding with $BrAc^-$ or as $(LaBrAc)^{++}$ colliding with $S_2O_3^=$ for reaction. The ternary complex $(LaBrAcS_2O_3)^\circ$ may also have a finite life-time. We consider it significant that B increases to a value (13.3) in the presence of La^{+++} which is substantially identical with B for the uncharged methyl ester-thiosulfate-ion reaction. In the next paper we direct attention to a similar state of affairs produced by lowering the dielectric constant to a point where ion-association becomes predominant in the absence of high valence ions. The reaction then behaves substantially as one between uncharged reactants.

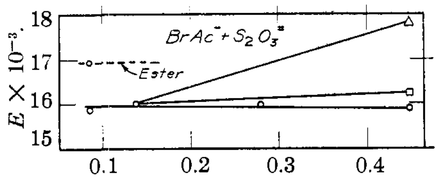

Fig. 3.—○, Sodium salts; □, $BaCl_2$ added; △, $LaCl_3$ added.

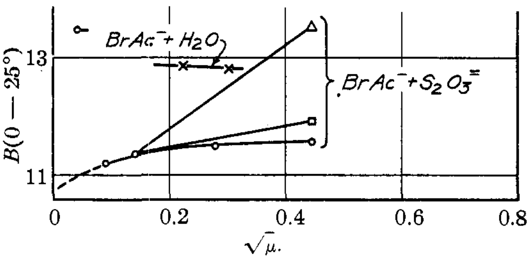

Fig. 4.—○-, Methyl ester-thiosulfate reaction; ○, reactants present as sodium salts; □, $BaCl_2$ added; △, $LaCl_3$ added.

In any case the highly abnormal local accumulation of reactant anions around a La^{+++} ion will operate to increase $\Delta\bar{L}_{act}$ well above the demands of the limiting law so that E_{act} will be increased. On the theory that the height of the energy barrier is the sole regulator of the rate of reaction, one would be tempted to predict that the rate should be decreased.

The clustering of the reactant anions about a central La^{+++} ion, however, provides a greatly enhanced opportunity for collisions between the bromoacetate and thiosulfate ions. This increase in total number of collisions will be reflected in $\Delta\bar{S}_{act}$, the increase in entropy of activation due to interionic attraction. In Section 2 it was shown that the limiting form of the Debye theory predicts that $\Delta\bar{S}_{act}/2.3R$ increases three times as rapidly as $\Delta\bar{L}_{act}/2.3RT$; it is reasonable to assume that a similar qualitative relation will hold in the high valence mixtures, even though an exact calculation cannot be made.[16]

Hence the increase in B is of sufficient magnitude to more than counterbalance the rate-depressing effect of an increase in E_{act}. The temperature dependence of these marked catalytic effects of high valence ions of sign opposite to the reacting ions furnishes convincing evidence of the importance of taking into account the variations in the entropy of activation as well as the energy of activation in developing a satisfactory theory of catalytic behavior. The previous theories appear to have neglected the most important factor.

Influence of Concentration and Temperature

A closer examination of the data reveals for $a = b = 0.005$ M where the reaction has been studied at 12.5° intervals that E_{act} decreases (see Fig. 5) by a small but significant amount (216 cal.), which of course is exactly paralleled by the decrease in B from 11.41 to 11.24. The parallel decrease in B[17] is a result of the relation $\partial E_{act}/\partial B = 2.3RT$ which holds when the solvent is constant. This decrease of E_{act} and B values with rising temperature is more definite in the data for

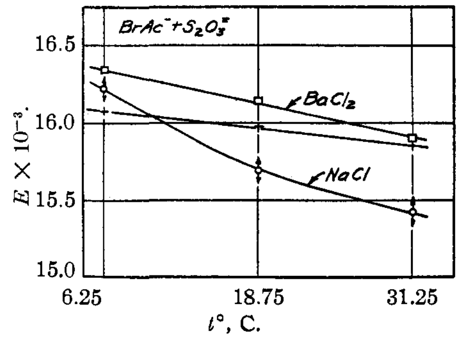

Fig. 5.—+ No added salt.

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[15] Fuoss and Kraus, THIS JOURNAL, series of papers from 1933 on; Fuoss, *Chem. Rev.*, **17**, 27 (1935).

[16] For the complications involved in the calculation, see La Mer and Parks [THIS JOURNAL, **55**, 4343 (1933)], particularly pages 4352-3.

[17] See Mary L. Miller, Thesis, Columbia University, 1934, for a more elaborate discussion of the necessity of parallel E and B values for a constant solvent at different temperature intervals.

0.18 M sodium chloride additions, where the heat capacity of activation is of the order of -12 cal./deg./mole (see Fig. 5).

In Eyring's theory,[18] which appeared after this work was completed, the activated complex is defined in terms of the partition function (sum of state) of the activated complex. In this theory the attempt is made to dispense completely with the concept of collisions and steric factors in reaction kinetics. Any changes in collision frequency, therefore, will be reflected entirely in terms of an entropy of activation. While this view has the advantage of being independent of any molecular picture, and may prove fruitful in the present case, we incline to the view supported by O. K. Rice and Gershinowitz that the collision mechanism has pictorial merit and should not be entirely discarded.[19]

Rodebush[20] has also pointed out that the collisional mechanism and Eyring's treatment are different but essentially equivalent ways of describing the same phenomenon, a conclusion which is evident from our eq. (4).

One may say, depending upon the point of view, that the reaction proceeds more rapidly as a result of an increase in the number of effective collisions, produced in the present data by an increase in the concentration of positive ions, or that the rate increases because of an increase in the entropy of activation,[21] which means that the number of systems crossing the energy barrier per unit of time is increased as a result of the increased number of reactive complexes per unit of volume of phase space.

Summary

1. An equation has been derived, based upon the limiting form of the Debye–Hückel theory, which predicts that E_{act}, the energy of activation of a reaction, and the entropy of activation (action constant B), will vary for water at 25° with the square root of ionic strength according to the law $E_{\text{act}}/2.3RT = E^0_{\text{act}}/2.3RT + 0.51\ Z_AZ_B\ \sqrt{\mu}$ and $B = B^0 + 1.52\ Z_AZ_B\ \sqrt{\mu}$.

2. The temperature coefficients of the reaction bromoacetate ion plus thiosulfate ion have been studied precisely over a range of temperature and concentration to obtain significant data for the effect of temperature and ionic environment upon E_{act} and B. For the sodium salts at $a = b = 0.005\ M$, $\partial E_{\text{act}}/\partial T = C_{\text{act}} \cong -8.6$ for the range 0–37.5°, in the presence of 0.18 M NaCl $C_{\text{act}} \cong -12$ cal./deg. mole.

3. The increase in log k produced by the addition of low valence ions (Na^+) is closely correlated with an increase in B.

4. In the presence of high valence ions (Ba^{++} and La^{+++}) of sign opposite to the reacting anions, E_{act} is considerably increased, but this retarding effect of an increase of height of the energy barrier is more than compensated for by an increase in the entropy of activation.

This example represents an interesting exception to the theory of catalytic action as usually stated and is discussed in the terms of the picture of ion-association.

NEW YORK, N. Y. RECEIVED AUGUST 15, 1935

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[18] Eyring, *J. Chem. Phys.*, **3**, 107 (1935). See also the very recent paper of Wynne-Jones and Eyring [*ibid.*, **3**, 492 (1935)] which reached us after this paper was written.

[19] O. K. Rice and Gershinowitz, *ibid.*, **2**, 273, 853 (1934); Evans and Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); *J. Chem. Phys.*, **3**, 479, 490 (1935).

[20] Rodebush, *J. Chem. Phys.*, **3**, 242 (1935).

[21] Brandsma appears to have been the first to identify the collision frequency and steric factors as entropy quantities. Brandsma, Thesis, Delft, 1925; *Rec. trav. chim.*, **47**, 94 (1928); **48**, 1205 (1929).