[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEMPLE UNIVERSITY]

The Persulfate Oxidation of Sulfoxides in Buffered Solution.[1] I

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The kinetics of the persulfate oxidation of water, diphenyl sulfoxide, thiodiglycol sulfoxide, diethyl sulfoxide and diethyl sulfide were investigated at 60 and 80° in buffered aqueous solutions of *p*H 8.0 and ionic strength 0.5. The rate of disappearance of persulfate was followed by iodometric titration. The reactions all were first order with respect to persulfate, and independent of the concentration of sulfur compound over the range studied. With the various substrates present the velocity of the reaction increased in the order in which the compounds are listed. Diethyl sulfone and thiodiglycol sulfone were isolated as oxidation products. Diethyl sulfide was oxidized to the sulfoxide at an immeasurably fast rate and thereafter to the sulfone at a rate identical with that observed for diethyl sulfoxide. At sulfoxide–persulfate molar ratios less than one, a point of inflection was observed in the first-order plots when diethyl or thiodiglycol sulfoxides were oxidized. The second portion of these reactions was interpreted as a further oxidative attack on the sulfone molecule, probably at the α-carbon. Activation energies were calculated for the reaction of persulfate with water and with the three sulfoxides. The value for water (32 kcal.) was considerably higher than the values for the sulfoxides (24–26 kcal.). It was observed that atmospheric oxygen had no effect on the rate. This was interpreted as evidence against a radical chain-type mechanism.

In the oxidation of mercaptans by potassium persulfate a maximum or limiting rate is attained above a certain initial concentration of sulfur compound.[3] Limited evidence indicates that the same is true when sulfides are oxidized.[4] In order to discover if this phenomenon extends to the persulfate oxidation of other type sulfur compounds, it was considered of interest to study the kinetics of the oxidation of organic sulfides and sulfoxides. It was hoped that an insight into the mode of oxidative attack at a sulfur atom would be gained, as well as some knowledge of the mechanism by which persulfate reacts.

The decomposition of potassium persulfate in aqueous solution, in which the persulfate is reduced to sulfate and the water is oxidized to oxygen, proceeds in dilute acid, neutral, or basic solution according to the over-all equation[5]

$$S_2O_8^= + H_2O \longrightarrow 2HSO_4^- + {}^1/_2O_2$$

The kinetics of this reaction has been studied extensively.[5–9]

Experimental

In this investigation kinetic runs were made at 60 and 80°, with an initial concentration of 0.02 *M* potassium persulfate, an ionic strength of 0.5, and the *p*H maintained at 8.0 by a phosphate buffer. The rate of disappearance of persulfate was followed by iodometric titration.

Constant Temperature Bath.—The temperature of the bath was determined using a calibrated thermometer. The temperature was 60.05 ± 0.02° for some of the kinetic runs and 80.20 ± 0.02° for others.

Buffer Solution.—0.0500 mole of reagent grade potassium dihydrogen phosphate and 0.0468 equivalent of standard sodium hydroxide solution were mixed together and made up to 1 liter with boiled distilled water.[10] The resulting solution was found to have a *p*H of 7.96 when tested with a *p*H meter.

Solution for Titration of Sample.—Sixty ml. of boiled distilled water and 10 ml. of 5.4 *M* sulfuric acid solution were mixed in a 500-ml. glass stoppered erlenmeyer flask. Ten ml. of a freshly prepared 1.2 *M* potassium iodide solution was added and then, with swirling, 2 g. of powdered sodium carbonate. These solutions were prepared just before they were needed.

Experimental Procedure.—The procedure for preparing the solutions used in the kinetic runs was as follows. C.P. grade potassium sulfate (1.721 g.) was weighed into a weighing bottle and quantitatively transferred to a 100-ml. volumetric flask. The purpose of the sulfate was to adjust the ionic strength to 0.5. The amount of sulfide or sulfoxide required to give the desired concentration was weighed into a weighing bottle and quantitatively transferred to the same volumetric flask. Enough buffer solution was then added to dissolve the sulfate and the organic sulfur compound, and the reaction solution was then made up to 100 ml. with more buffer solution. The flask was thoroughly shaken, then stoppered and immersed in the constant temperature bath and allowed to reach equilibrium.

An amount of reagent grade potassium persulfate necessary to make the solution 0.02 *M* in persulfate (0.541 g.) was placed in a 250-ml. round-bottom, ground-glass stoppered reaction flask which was then immersed in the constant temperature bath. After five minutes, the contents of the volumetric flask was carefully poured into the reaction vessel containing the solid persulfate. The time of mixing was noted and recorded.

Soon after the start of the reaction, a 10-ml. sample of the reaction solution was withdrawn with a previously calibrated pipet and discharged into a flask containing the solution for the titration of the sample. The time of withdrawal of the sample was recorded as the time when half of the sample had run from the pipet. A trace of solid ferrous sulfate was added to the solution to catalyze the reaction of persulfate ion with iodide ion. The flask was stoppered and placed in the dark, and, after 30 minutes, 120 ml. of boiled, distilled water was added and the solution titrated with a standard 0.01 *N* thiosulfate solution using starch as the indicator.

Diethyl Sulfide.—This compound was redistilled fractionally through a column packed with Berl saddles. The water-clear fraction boiling between 92.0 and 92.2° was collected and stored in the dark in a glass stoppered bottle.

Diethyl Sulfoxide.—Equimolar quantities of diethyl sulfide and 30% hydrogen peroxide solution were dissolved in acetone and the mixture was allowed to stand for two days at room temperature.[11] The acetone was removed by distillation and the remaining solution of the sulfoxide in water was subjected to vacuum distillation to remove the water. From the amber-colored residue diethyl sulfoxide was obtained as a water-clear sirupy distillate which boiled at 88–91° (12 mm.).

Diphenyl Sulfoxide.—Starting with diphenyl sulfide, the same procedure was followed as for the preparation of diethyl sulfoxide. On removing the acetone, there remained a residue of crude diphenyl sulfoxide, which was recrystallized from petroleum ether, m.p. 69–70°.

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(1) Taken from the Ph.D. dissertation of Leonard S. Levitt.

(2) Department of Chemistry, Stevens Institute of Technology, Hoboken, N. J.

(3) R. L. Eager and C. A. Winkler, *Can. J. Research*, [B] **26**, 527 (1948).

(4) E. Larsson, *Trans. Chalmers Univ. Technol., Gothenberg*, **87**, 23 (1949).

(5) A. Kailan and L. Olbrich, *Monatsh.*, **47**, 449 (1926).

(6) H. Palme, *Z. anorg. allgem. Chem.*, **112**, 97 (1920).

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(8) H. G. Levi and E. Migliorini, *Gazz. chim. ital.*, **36**, [II] 599 (1906).

(9) L. Green and O. Masson, *J. Chem. Soc.*, 2083 (1910).

(10) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, 1949, p. 1127.

(11) R. L. Shriner, H. C. Struck and W. J. Jorison, THIS JOURNAL, **52**, 2060 (1930).

Thiodiglycol Sulfoxide.—This compound was prepared from thiodiglycol in the same manner employed for the other sulfoxides. It was not necessary in this case to remove the acetone by distillation, for a mass of white crystal had formed in the flask after standing for two days. The supernatant solution was simply poured off, and the product was recrystallized from an acetone–water mixture, m.p. 108°.

Isolation of the Oxidation Products.—Although aqueous persulfate has been used for the actual preparation of sulfoxides and sulfones from the corresponding sulfides,[4] it was thought advisable in the present work to ascertain if these were the products in the kinetic runs. To this end, 100 ml. each of three reaction mixtures containing, respectively, diethyl sulfoxide, thiodiglycol sulfoxide and diphenyl sulfoxide were prepared with *p*H, ionic strength and persulfate concentration the same as in the rate studies. The sulfoxide concentrations were 0.02, 0.02 and 0.01[12] *M*, respectively, and the reaction temperatures 80, 76 and 80°, respectively. The reactions were each terminated at a time corresponding approximately to their half-time periods.

The solution containing diphenyl sulfoxide had become opaque with a white colloidal suspension in the same manner that it had in the kinetic runs. The other two solutions, however, remained clear and colorless. Each of the solutions was concentrated by evaporation on a steam-bath, and then extracted with ether. On evaporation of the ether extracts from the solution of diethyl sulfoxide and of thiodiglycol sulfoxide, white solids remained in both cases. The products were recrystallized from ether. Diethyl sulfone was obtained as a white crystalline material melting at 70°, and thiodiglycol sulfone as a white waxy solid melting at 59°. The colloidal suspension remaining as the oxidation product of diphenyl sulfoxide could not be extracted by ether, benzene, ligroin, chloroform or carbon tetrachloride. The substance was steam distillable, but could not be separated from the water. Hence, it was neither isolated nor identified.

Results and Discussion

In all of the kinetic runs, the initial concentration of potassium persulfate was 0.02 *M*, the ionic strength was 0.5 and the *p*H was maintained at 8.0 by a phosphate buffer. Hence, the rate of reaction could not be affected during the course of an experiment by an increase in acidity nor by a significant increase in ionic strength, both of which do occur when potassium persulfate decomposes in pure water. Thus, from the outset, three variables which could have a marked effect on the velocity of the reaction were eliminated.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF $K_2S_2O_8$ (0.02 *M*) AT 60° IN AQUEOUS SOLUTIONS OF *p*H 8.0 AND IONIC STRENGTH 0.5

Substrate	Concn., *M*	$t_{1/2}$, hr.	k, hr.$^{-1}$	k_c, hr.$^{-1}$
Water	55.5	39.4	0.0176	0.0176
Diethyl sulfide	0.020	6.66	.104	.086
Diethyl sulfoxide	.020	6.39	.108	.090
Thiodiglycol sulfoxide	.010	6.42	.108	.090
Diphenyl sulfoxide	.0075	27.5	.0252	.0076

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF $K_2S_2O_8$ (0.02 *M*) AT 80° IN AQUEOUS SOLUTIONS OF *p*H 8.0 AND IONIC STRENGTH 0.5

Substrate	Concn., *M*	$t_{1/2}$, hr.	k, hr.$^{-1}$	k_c, hr.$^{-1}$
Water	55.5	2.52	0.275	0.275
	55.5	2.55	0.272	.272
Diethyl sulfide	0.020	0.65	1.07	.80
	.020	.63	1.09	.82
Diethyl sulfoxide	.020[a]	.65	1.07	.80
	.020	.63	1.09	.82
	.015[a]	.64	1.08	.81
	.010	.64	1.08	.81
Thiodiglycol sulfoxide	.010	.70	0.99	.72
Diphenyl sulfoxide	.010	2.05	.338	.064
	.0075	2.06	.337	.063

[a] Under an atmosphere of nitrogen.

Order of Reaction with Respect to Persulfate.—It is immediately apparent from the accompanying plots (Figs. 1 and 2) of the logarithm of the persulfate concentration *vs.* time, that the reaction is

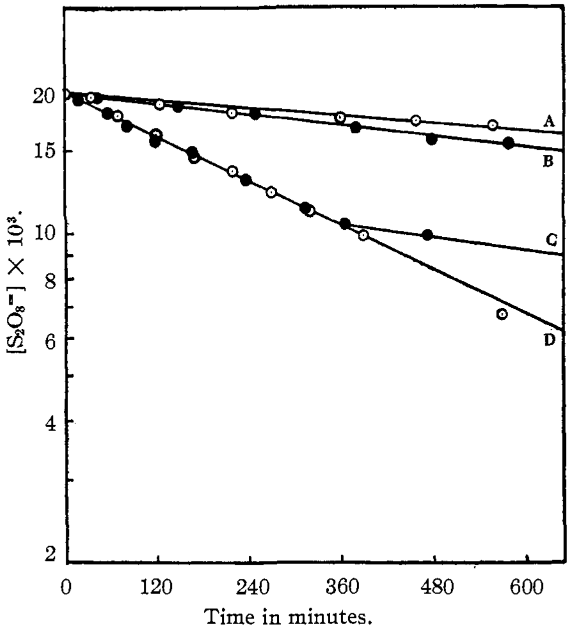

Fig. 1.—Persulfate oxidation at 60° of: A, water; B, diphenyl sulfoxide, 0.0075 *M;* C, thiodiglycol sulfoxide, 0.01 *M;* D, diethyl sulfoxide, 0.02 *M*.

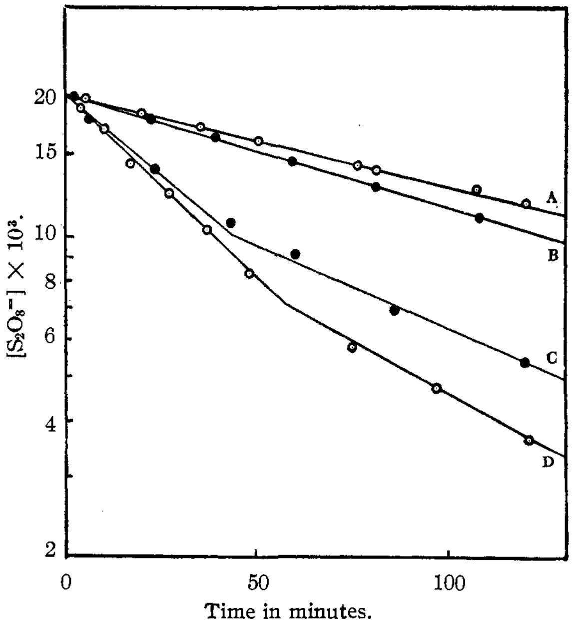

Fig. 2.—Persulfate oxidation at 80° of: A, water; B, diphenyl sulfoxide, 0.01 *M;* C, thiodiglycol sulfoxide, 0.01 *M;* D, diethyl sulfoxide, 0.01 *M*.

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[12] The limit of solubility of diphenyl sulfoxide under these conditions.

first-order with respect to the disappearance of persulfate. The reaction rate constant for a given experiment was calculated from the slope of the line and also from the half-time, both of which were obtained from the logarithmic plot of the data. Tables I and II summarize the results obtained in 16 experiments.

The reproducibility of the value for the kinetic constant in duplicate experiments is seen to be quite satisfactory. When consecutive samples were taken a few minutes apart from reactions which were proceeding extremely slowly (the oxidation of water and of diphenyl sulfoxide at 60°) their titration values differed by only a drop or two of sodium thiosulfate solution.

The Oxidation of Water by Persulfate.—The first-order rate constant for the oxidation of water by potassium persulfate under the conditions used in this investigation was found to be 0.274 hr.$^{-1}$ at 80°. This value is to be compared with that observed at the same temperature in previous investigations, such as 0.300,[9] 0.346[7] and 0.428,[13] which were measured under different conditions of *p*H, ionic strength and initial concentration of persulfate. The retarding effect on the rate brought about by high concentrations of potassium and sulfate ions[5] probably accounts for the lower value observed in this research. The rate constant 0.0176 hr.$^{-1}$ obtained at 60° in the present work may be compared with the value 0.0164 hr.$^{-1}$ at 56°.[8]

Oxidation of Sulfur Compounds.—When diphenyl sulfoxide, diethyl sulfoxide, thiodiglycol sulfoxide or diethyl sulfide was present in the aqueous solution of potassium persulfate, the reaction proceeded at a faster rate but was still first order with respect to persulfate (Figs. 1 and 2). In these solutions it is logical to assume that the persulfate is consumed by means of two simultaneous reactions: oxidation of the sulfur compound and oxidation of water. Hence, the value of the rate constant for the water reaction (0.274) should be subtracted from those rate constants which in reality represent the sum of two processes. The remainder should be the rate constant to be associated with the oxidation of the sulfur compound alone. Thus, if $-dc/dt = k_a c + k_b c$, then $\ln c_0/c = (k_a + k_b)t$, where $(k_a + k_b)$ is the sum of the rate constants for two simultaneous reactions by which c may be consumed. The rate constant obtained in this manner will be designated k_c, the "corrected" rate constant. Values for k_c will be found in Tables I and II together with the observed over-all rate constants k.

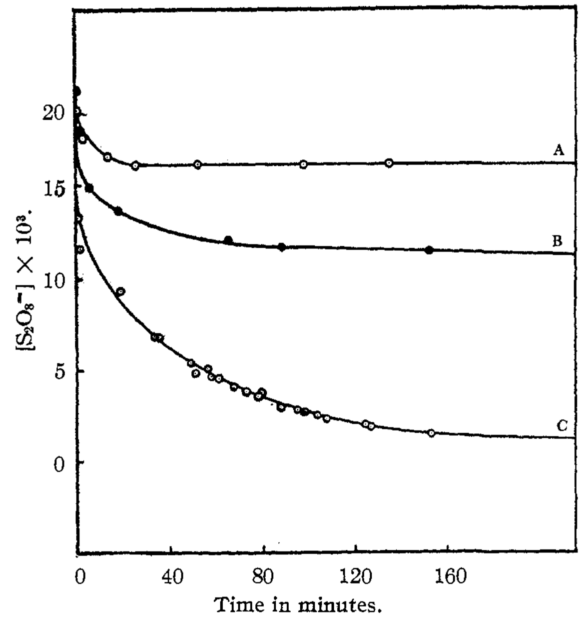

Fig. 3.—Disappearance curves for persulfate in the oxidation of diethyl sulfide, 0.02 *M*, at: A, 30°; B, 60°; C, 80° (composite of 2 runs).

Although we have shown that diethyl sulfoxide and thiodiglycol sulfoxide are oxidized to the corresponding sulfones under the conditions of the kinetic studies, we have not succeeded in identifying diphenyl sulfone as the oxidation product of diphenyl sulfoxide. It seems probable that it is, at least, among the products, but, nevertheless, attack at the benzene ring is not unlikely (Elbs persulfate oxidation). In the case of thiodiglycol sulfoxide, it is interesting to note that oxidation occurs at partially oxidized sulfur in preference to partially oxidized carbon.

No attempt was made to isolate the products of the oxidation of ethyl sulfide. From the very rapid disappearance of persulfate at the beginning of the reaction (Fig. 3) and its subsequent disappearance at both 60 and 80° at a rate identical with that observed in the oxidation of diethyl sulfoxide (Tables I and II), it is obvious that the sequence of reactions taking place must be sulfide → sulfoxide → sulfone. From the data at 30° (curve A, Fig. 3) a rough estimate of the rate constant for the oxidation of diethyl sulfide to the sulfoxide at this temperature is 2.8 hr.$^{-1}$. The disappearance curve at 30° shows that after all the sulfide has been consumed, the subsequent oxidation of the sulfoxide proceeds immeasurably slowly.

Points of Inflection.—At sulfoxide–persulfate molar ratios less than one, when diethyl or thiodiglycol sulfoxides were used, the first-order plots show a break in the curve in approximately the region where the stoichiometry predicts that all the sulfoxide has been consumed (for example, Figs. 1 and 2, curves C). Thus it would appear that persulfate oxidizes an equimolar quantity of sulfoxide to sulfone. The over-all equation for these reactions, therefore, can be written

$$R_2SO + S_2O_8^{=} + 2OH^- \longrightarrow R_2SO_2 + 2SO_4^{=} + H_2O$$

The second straight-line portion of these curves apparently represents the rate of oxidative attack on the sulfone molecule, possibly at the α-carbon. (Removal of α-hydrogen during the oxidation of ethers has been proved.[14]) Table III gives the rate constant, k', measured for the second portion of the reactions. The corrected value, k'_c, is also included.

Activation Energies.—Application of the Arrhenius equation to the data obtained for the corrected rate constants (k_c) at 60 and 80° permits the evaluation of the activation energy for each of the

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[13] P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

[14] M. Cass, THIS JOURNAL, **69**, 500 (1947).

TABLE III

THE RATE CONSTANT k' FOR THE OXIDATION OF SULFONES AT 80°

Original substrate	Concn., M	k', hr.$^{-1}$	k_0', hr.$^{-1}$
Diethyl sulfide	0.02	0.69	0.42
	.02	.67	.40
Diethyl sulfoxide	.02	.61	.34
	.01	.63	.36
Thiodiglycol sulfoxide	.01	.56	.29

reactions studied in this investigation. The results are presented in Table IV.

TABLE IV

ACTIVATION ENERGIES

Substrate	Concn., M	k_0, hr.$^{-1}$ 30°	80°	Act. en., kcal./mole
Water	55.5	0.0176	0.274	32.1
Diethyl sulfoxide	0.02	.090	.81	25.6
Thiodiglycol sulfoxide	.01	.090	.72	24.2
Diphenyl sulfoxide	.0075	.0076	.063	24.7

It is seen that the activation energy for the oxidation of the sulfoxides is nearly the same for the three compounds studied, and they are considerably less than the value for the oxidation of water. The average value of 24.8 kcal. for the three sulfoxides may be compared with the 26 kcal. observed in the persulfate oxidation of mercaptans.[3] The value for the water reaction is quite close to the average value of 34 kcal., which may be estimated from the data obtained by previous investigators under similar conditions.[6,8,9]

Effect of Oxygen on the Rate.—Two kinetic runs were made in which the reaction mixture was saturated with pure nitrogen and kept under an atmosphere of the gas throughout the experiment (Table II). The fact that the rate under these conditions is identical with those obtained in the presence of atmospheric oxygen indicates that the reaction is neither inhibited, retarded nor accelerated by oxygen. This affords evidence, though not of a conclusive nature, against a radical chain-type mechanism for the reactions studied.

Effect of Structure of the Compound Oxidized.—It is apparent from Fig. 2 and Table II that at 80° the oxidation of diethyl sulfoxide proceeds at a slightly faster rate than that of thiodiglycol sulfoxide, and that both of these compounds are oxidized much more rapidly than is diphenyl sulfoxide. These results are similar to those observed in the oxidation of sulfides by potassium persulfate[4] and by hydrogen peroxide.[15]

It would appear that an inductive effect is operative when a hydroxy, phenyl or chloro[15] group is present in the molecule close to the sulfur atom. By attracting electrons, negative groups such as these can effectively decrease the electron density at the sulfur atom, thus rendering the electrons less available for formation of a coördinate bond with an oxygen atom or for extraction by an oxidizing agent.

Effect of Sulfoxide Concentration.—Over the range of concentration studied in the above experiments, the rate of disappearance of persulfate is apparently independent of the concentration of the sulfur compound oxidized. The effect of much lower concentrations of sulfoxide on the rate will be presented in a future paper.

[15] K. Ishida, *J. Chem. Soc. Japan*, **64**, 242 (1943).

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Metal–Water Reactions. II. Kinetics of the Reaction between Lithium and Water Vapor

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The rate of the reaction between lithium metal and water vapor has been studied from 45.0 to 75.0°. The reaction was found to proceed according to a logarithmic rate law. The rate constant was independent of water vapor pressure over a range of 22 to 55 mm. The energy of activation for the reaction was found to be 6.2 to 5.5 kcal./mole, depending on the water vapor pressure.

Introduction

The kinetics of metal–gas reactions involving O_2, N_2 and H_2 have been widely studied and numerous references are available.[2] However, few studies have been reported on water vapor–metal reactions and none using the more active metals.

A study of the rate at which reaction takes place between lithium and water vapor was undertaken as the second in a series which compares water vapor–metal reactions with other gas–metal reactions. Since the lithium reaction takes place according to the equation

$$2Li + 2HOH = 2LiOH + H_2$$

the rate of reaction was followed by observing the evolution of H_2 as a function of time under several water vapor concentrations.

It has been observed that the reaction of a gas with a metal may proceed according to one of several laws[3]

(I) the linear law $w = kt$
(II) the parabolic law $w^2 = kt$
(III) the logarithmic law $w = k \log (1 + at)$

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys," Academic Press, Inc., New York, N. Y., 1953.

[3] E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).