droxide decreases the solubility of all the solid phases. At 350° the solubilities of the various phases are increased markedly.

COLLEGE PARK, MD. RECEIVED MAY 15, 1937

[CONTRIBUTION FROM THE EASTERN EXPERIMENT STATION, U. S. BUREAU OF MINES]

Solubility Equilibria of Sodium Sulfate at Temperatures from 150 to 350°.[1] IV. Comparison of Evaporation and Equilibrium Solubility Values

BY W. C. SCHROEDER,[2] A. A. BERK[3] AND EVERETT P. PARTRIDGE[4]

The first three papers of this series have presented data for the solubility of sodium sulfate in solutions containing sodium hydroxide, sodium chloride, sodium carbonate and sodium phosphate at temperatures above 100°.[5-7] The utility of this information should be increased materially by the determination of the degree of accuracy with which the equilibrium values can be applied to a system undergoing evaporation. In this paper comparison is made between the amount of sodium sulfate in a solution from which steam is being removed, and the amount of sodium sulfate present in the same solution at equilibrium. The test temperatures were approximately 200, 250, 300 and 350°.

Evaporation Bomb and Test Procedure.—The equipment used in these evaporation tests is shown in Fig. 1. It consisted of a nickel bomb equipped with four samplers for taking solution samples, two of which are indicated in the drawing. Heat for evaporation was supplied by a heater inserted into a tube in the bottom. The bomb body proper was enclosed in an air thermostat. The ends of the samplers protruded from the thermostat, permitting the use of the flat gasket of rubber composition shown in the diagram, without danger from carbonization.

In operation of the bomb it was charged with the desired solution, about 75% saturated with sodium sulfate and containing 300 to 350 g. of water. This solution was heated to the boiling point and put into the bomb which previously had been heated to 100°; the bomb was immediately put into the thermostat and brought up to temperature, preventing any possible crystallization of sodium sulfate from the solution before evaporation was begun. With a constant rate of heat input to the heater steam was led off through the needle valve to maintain constant pressure. The first sample was taken after removal of 3 to 5 g. of water more than the amount necessary to produce saturation and the other samples were taken at various subsequent periods during the evaporation. After the last sampling, the remaining solution was blown out through the drain plug shown in the side of the bomb or evaporation was continued to dryness.

The temperature could be maintained easily within 2° of any desired value. In all of the runs the rate of energy input to the hot tube in the bottom of the bomb was

TABLE I

COMPARISON OF EVAPORATION AND EQUILIBRIUM SOLUBILITY VALUES FOR SODIUM SULFATE IN WATER: SOLID PHASE, SODIUM SULFATE

Run	Sample	Temp., °C.	Pressure[a] lb./sq. in.	Na_2SO_4, g./100 g. H_2O Evapn.	Soly.[b]	Scale thickness, inch[c]
4	1	197	200	46.3	44.5	0.11
	2	197	200	44.8	44.5	
	3	196	205	45.0	44.5	
	4	196	200	44.0	44.5	
18	1	201	210	46.0	44.5	.09
	2	201	205	45.6	44.5	
	3	200	200	45.4	44.5	
	4	199	200	44.8	44.5	
20	1	224	330	2.02[d]	45.5	.14
	2	224	320	45.5	45.5	
	3	225	330	45.2	45.5	
19	1	228	360	47.7	45.7	.08
	2	226	360	45.0	45.5	
	3	225	350	44.7	45.5	
2	1	272	820	36.7	38.0	.18
	2	273	820	36.0	38.0	
	3	272	815	35.8	38.0	
	4	272	820	35.3	38.0	
3	1	310	1400	17.6	18.2	.09
	2	310	1400	17.8	18.2	
	3	309	1400	17.3	18.2	
	4	309	1400	18.1	18.2	
14	1	347	2325	2.6	2.8	.006
	2	347	2300	2.7	2.8	
	3	347	2325	2.9	2.8	

[a] Read from gage attached to bomb. [b] Value from solubility curves. [c] Approximate maximum thickness. [d] Sample in error.

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(5) W. C. Schroeder, Alton Gabriel and Everett P. Partridge, THIS JOURNAL, **57**, 1539–1546 (1935).

(6) W. C. Schroeder, A. A. Berk and Alton Gabriel, *ibid.*, **58**, 843–849 (1936).

(7) W. C. Schroeder, A. A. Berk and Alton Gabriel, *ibid.*, **59**, 1783 (1937).

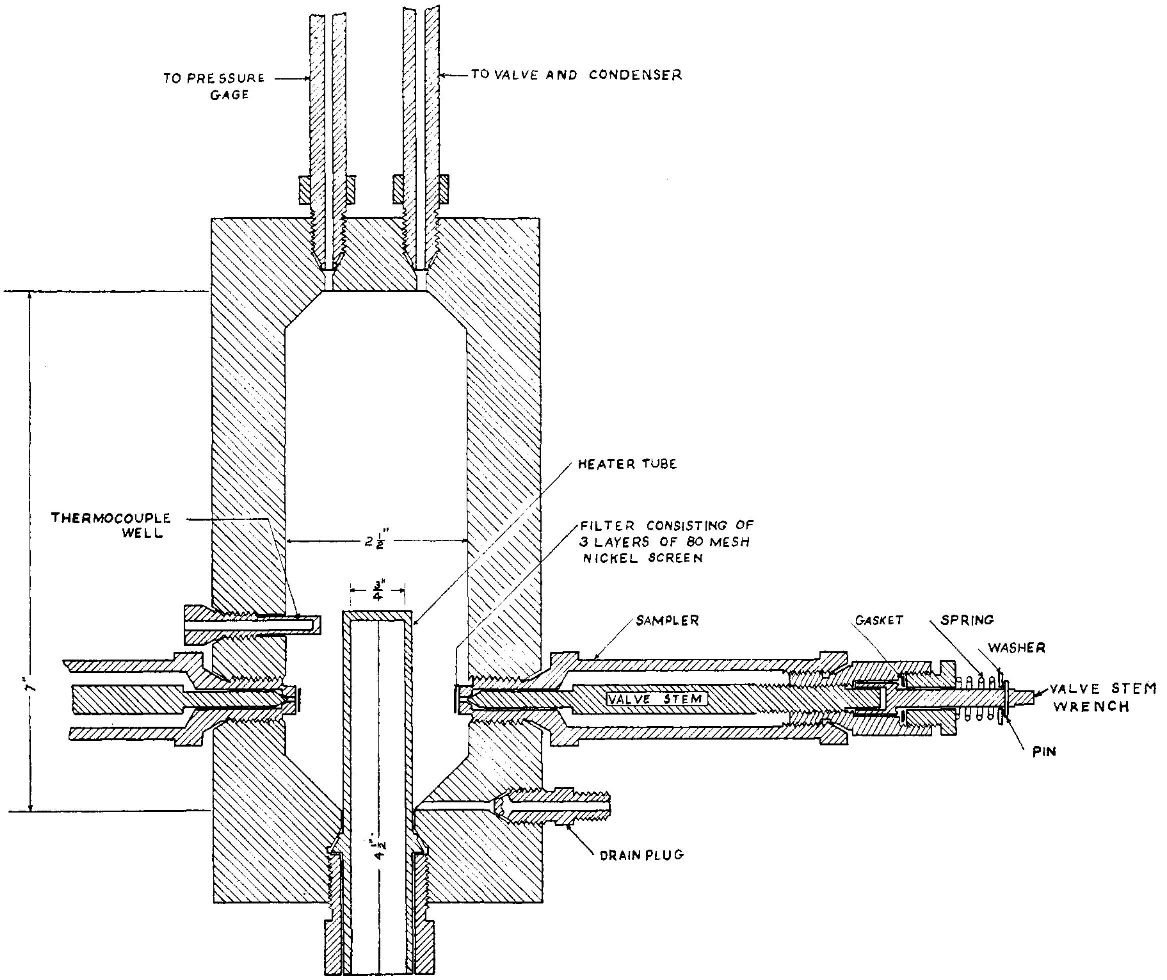

Fig. 1.—Evaporation bomb.

100 watts, which gave a rate of evaporation of approximately 180 g. of water per hour at the lower pressures and a somewhat higher rate at the higher pressures due to the lower latent heat of vaporization.

After each test the heater tube was removed from the bottom of the bomb, and if any scale was present on its surface the thickness was measured and the mechanical structure noted.

Comparison of Evaporation and Equilibrium Solubility Values

Table I gives the data for the amount of sodium sulfate in water solution in the evaporation bomb at temperatures between approximately 200 and 350°. Comparison with the equilibrium solubility values indicates general agreement within 1 g. of sodium sulfate per 100 g. of water. The maximum deviation at 272° was somewhat greater than this and may indicate that the value secured in the solubility studies was slightly high at this temperature. It safely may be concluded, however, that sodium sulfate in water does not show any marked tendency to supersaturation.

Table II gives the results of evaporation tests with solutions containing sodium hydroxide and sodium sulfate. No appreciable supersaturation is indicated. The same result was obtained for sodium sulfate in solutions of sodium chloride as shown in Table III.

Table IV compares the evaporation and solubility values for solutions containing sodium carbonate and sodium sulfate. For the two runs at 200° appreciable supersaturation is evident although at 250 and 350° this effect has diminished greatly or disappeared. The solid phase was a double salt of sodium carbonate and sodium sulfate ($Na_2CO_3 \cdot 2Na_2SO_4$) in all of the runs except the last one. As shown in the second paper[6] this double salt forms solid solutions with either sodium carbonate or sodium sulfate depending on the solution composition. The solid

TABLE II

COMPARISON OF EVAPORATION AND EQUILIBRIUM SOLUBILITY VALUES FOR SODIUM SULFATE IN SOLUTIONS OF SODIUM HYDROXIDE, SOLID PHASE, SODIUM SULFATE

Run	Sample	Temp., °C.	Pressure, lb./sq. in.[a]	G./100 g. H_2O			Scale thickness, inch[c]
				NaOH	Na_2SO_4 Evapn.	Na_2SO_4 Soly.[b]	
5	1	200	195	8.4	32.7	31.6	No scale
	2	200	195	8.9	32.2	31.3	
	3	199	190	10.9	30.0	29.5	
	4	203	195	17.8	24.8	24.2	
6	1	251	520	9.7	35.5	34.8	0.060
	2	250	515	10.1	34.6	34.7	
	4	249	490	17.7	31.9	31.0	
7	1	294	1030	5.5	31.6	29.9	Scale formed
	2	293	1020	8.2	31.7	31.7	Thickness not measured
	4	294	1020	6.0[d]	32.1	30.4	
15	1	350	2375	1.2	3.3	3.7	No scale
	2	350	2360	1.3	3.4	3.8	
	3	350	2375	1.6	3.5	4.3	
	4	350	2350	2.7	5.5	6.0	

[a] Read from gage attached to bomb. [b] Value from solubility curves. [c] Approximate maximum thickness. [d] Sample in error.

TABLE III

COMPARISON OF EVAPORATION AND EQUILIBRIUM SOLUBILITY VALUES FOR SODIUM SULFATE IN SOLUTIONS OF SODIUM CHLORIDE, SOLID PHASE, SODIUM SULFATE

Run	Sample	Temp., °C.	Pressure lb./sq. in.[a]	G./100 g. H_2O			Scale thickness, inch[c]
				NaCl	Na_2SO_4 Evapn.	Na_2SO_4 Soly.[b]	
8	2	200	202	5.8	34.5	34.5	Evidence of thin layer of scale
	3	200	202	7.0	33.4	32.5	
	4	200	200	10.2	28.5	28.3	
9	1	250	540	5.5	33.4	33.5	0.035
	2	249	540	5.9	32.6	32.7	
	4	249	540	7.2	30.6	31.0	
10	1	299	1180	5.4	19.7	19.6	.050
	2	299	1165	5.7	19.5	19.5	
	3	300	1160	7.4	18.5	18.7	
	4	300	1160	14.6	17.4	17.5	
16	1	351	2350	6.2	5.0	5.5	No scale
	2	350	2325	6.7	5.3	5.7	
	3	350	2300	8.7	6.8	6.8	
	4	351	2340	13.4	8.8	9.0	

[a] Read from gage attached to bomb. [b] Value from solubility curves. [c] Approximate maximum thickness.

phase in the last run was a mixture of sodium sulfate and solid solution of sodium sulfate in the double salt.

Table V compares the equilibrium solubility values and the evaporation values for sodium sulfate in solutions of sodium phosphate. In those runs in which sodium sulfate was present as the solid phase there is no evidence of supersaturation, and run 28 gave values somewhat below those found in the solubility determinations. Run 23 indicated marked supersaturation when the double salt $Na_2SO_4 \cdot 2Na_3PO_4$ was present in the solid phase. The solid in the bomb at the end of this run was largely $Na_2SO_4 \cdot 2Na_3PO_4$ but there was a small amount of $Na_2SO_4 \cdot 5Na_3PO_4$ resulting about the time sample 3 was taken since a change in phase would be anticipated at the concentrations shown by this sample. The solid present in Run 26 was largely the isotropic phase described in the third paper of this series.[7]

Scale Formation

Examination of Tables I to V inclusive will show that a definite scale was formed on the surface of the hot tube in 23 out of the 26 runs. These scales were dense and hard, of considerable mechanical strength, and very similar in appearance to those formed by calcium sulfate in boiler operation.

TABLE IV

COMPARISON OF EVAPORATION AND EQUILIBRIUM SOLUBILITY VALUES FOR SODIUM SULFATE IN SOLUTIONS OF SODIUM CARBONATE

Run	Sample	Temp., °C.	Pressure[a] lb./sq. in.	G./100 g. H_2O			Solid phase	Scale thickness, inch[c]
				Na_2CO_3	Na_2SO_4 Evapn.	Na_2SO_4 Soly.[b]		
11	1	201	210	4.9[d]	28.5	28.2	$Na_2CO_3 \cdot 2Na_2SO_4$	0.025
	2	201	210	5.2	29.9	27.5		
	3	200	205	5.7	33.8	24.0		
	4	200	205	3.5	34.5	32.5		
13	1	202	220	5.0	28.7	28.0	$Na_2CO_3 \cdot 2Na_2SO_4$	.010
	2	203	220	5.1	30.1	28.0		
	4	199	205	2.9	37.1	34.5		
12	1	250	560	5.0	23.4	22.0	$Na_2CO_3 \cdot 2Na_2SO_4$	.065
	2	250	550	5.3	24.5	21.2		
	3	250	555	4.6	23.6	23.0		
	4	250	555	3.8	26.7	25.5		
17	1	354	2525	0.63	1.0	1.7	$Na_2CO_3 \cdot 2Na_2SO_4$ + Na_2SO_4	.011
	2	353	2500	.75	1.1	1.7		
	3	354	2475	.79	1.2	1.7		

[a] Read from gage attached to bomb. [b] Value from solubility curves. [c] Approximate maximum thickness. [d] Hydroxide present from hydrolysis of carbonate less than 0.5 g. per 100 g. of H_2O in all cases.

TABLE V

COMPARISON OF EVAPORATION AND EQUILIBRIUM SOLUBILITY VALUES FOR SODIUM SULFATE IN SOLUTIONS OF SODIUM PHOSPHATE

Run	Sample	Temp., °C.	Pressure[a] lb./sq. in.	G./100 g. H_2O			Solid phase	Scale thickness, inch[c]
				Na_3PO_4	Na_2SO_4 Evapn.	Na_2SO_4 Soly.[b]		
22	1	202	195	5.0	45.2	45.0	Na_2SO_4	0.090
	2	201	195	5.6	45.6	45.0		
	3	199	190	6.0	45.6	45.0		
	4	200	190	6.8	45.4	45.2		
23	1	202	190	25.8	25.7	23.0	$Na_2SO_4 \cdot 2Na_3PO_4$	.160
	3	201	190	28.5	30.7	19.0		
	4	201	190	27.2	31.0	20.5		
24	1	247	510	4.3	46.7	47.0	Na_2SO_4	.180
	2	246	510	4.5	46.8	47.0		
	4	246	510	5.9	47.6	47.8		
26	1	251	545	7.2	26.7	Vertical soly. curve	Isotropic double salt or solid soln.	.160
	2	251	540	8.5	28.4			
	3	250	540	8.2	31.6			
	4	250	540	8.6	35.8			
28	1	298	1160	1.6	26.6	29	Na_2SO_4	.150
	2	298	1160	1.7	28.0	30		
	3	298	1160	1.8	28.7	30		
	4	298	1160	2.0	28.9	31		
27	1	308	1140	3.3	32.9	34	Na_2SO_4	.110
	2	308	1140	3.6	35.0	34.5		
29	1	349	2360	0.15	2.2	Soly. not detd.	Na_2SO_4	.013
	2	349	2365	.17	2.5			
	3	349	2360	.20	2.5			
	4	350	2365	.26	2.5			

[a] Read from gage attached to bomb. [b] Value from solubility curves, approximate maximum thickness. [c] Approximate maximum thickness.

The present theories of scale formation imply that solids which show an increase in solubility with increase in temperature should separate from the solution as sludge and those which show a decrease with temperature may deposit as scale on a heating surface.[8,9] In most of the runs in

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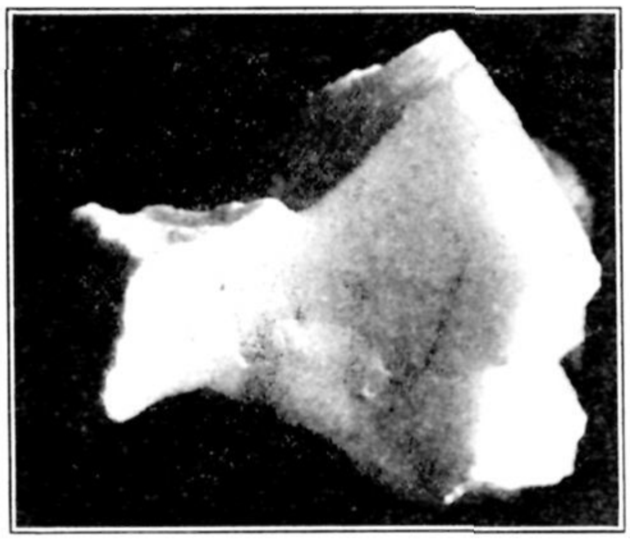
(8) R. E. Hall, "A Physico-Chemical Study of Scale Formation and Boiler-Water Conditioning," Carnegie Institute of Technology, Bulletin No. 24, pp. 20–22.

(9) E. P. Partridge, "Formation and Properties of Boiler Scale," Dept. of Engineering Research, University of Michigan, Bulletin No. 15, pp. 67–87.

which scale was formed this relationship will be found to hold. In Table I, however, scale was formed in runs 4, 18, 19 and 20 with sodium sulfate, in the range in which its solubility increases with temperature.

Cross section.



Inner surface.

Fig. 2.—Sodium chloride scale formed at 300°.

Since all four of these runs were conducted near temperatures at which sodium sulfate changes form, (Na_2SO_4 V to Na_2SO_4 III or Na_2SO_4 III to Na_2SO_4 I), it is possible that a shift from equilibrium with respect to an unstable phase to equilibrium with respect to a stable phase might partly account for the scale formation. This possibility could be tested readily by a run with sodium chloride since this salt seems to suffer no change in phase from 0 to 350°. Furthermore, at 300°, the temperature of the test, the salt shows a rapid increase in solubility with temperature and according to the theory should not form scale. Sodium chloride, however, formed a heavy layer of scale approximately 0.32 inch (8 mm.) thick during the evaporation of 275 cc. of water. Figure 2 is a picture indicating the thickness and appearance of the inner surface of this scale. It had a density of 2 compared with a theoretical value of 2.16 for solid sodium chloride. No pores were visible under the microscope at high magnification.

While it may be possible to predict the scaling characteristics of the more insoluble salts usually encountered in boiler operation from the decrease in solubility with increase in temperature, the highly soluble salts apparently do not conform. Partridge has suggested previously[9] that "At high rates of heat transfer, there might be deposited by bubble evolution, not only any substance with a negative solubility slope but also, conceivably, a substance whose solubility increases with increase in temperature." This suggestion was intended to apply in the main to salts of low solubility, but with salts of high solubility, such as sodium sulfate and sodium chloride, a small amount of vaporization at the heat transfer surface would tend to throw out a considerable amount of solid and cause scale formation even at low rates of heat transfer.

These tests are not sufficiently comprehensive to form a basis for the modification of the present theory, but they do indicate that factors other than the slope of the solubility–temperature curve can be of importance in scaling. Such factors may be the amount of salt in a unit of solution, the crystallographic characteristics of the solid, as well as the degree of supersaturation during the short contact with the heating surface. The scale forming characteristics of different salts might well be subjected to further investigation in order that an accurate and comprehensive theory may be formulated.

Acknowledgments.—This paper completes the presentation of the data that have been collected on the solubility of sodium sulfate and other soluble salts at high temperature. The authors wish to thank the contributors and the Joint Research Committee on Boiler Feedwater Studies who have made this investigation possible, and to thank Mr. J. H. Walker, chairman of the committee, for his many constructive suggestions.

Conclusions

1. The removal of steam from a solution containing sodium sulfate alone, or sodium sulfate in the presence of sodium hydroxide, sodium chlo-

ride, sodium carbonate, or sodium phosphate does not cause supersaturation with respect to sodium sulfate as long as this salt is the only solid phase.

2. If the solid phase deposited from these solutions is a double salt of sodium sulfate and sodium carbonate, or sodium sulfate and sodium phosphate marked supersaturation may be encountered.

3. Sodium sulfate and sodium chloride have formed heavy scales in the region in which the solubility increases with temperature.

4. The evaporation tests have furnished additional information concerning the solubility of sodium sulfate, and except where supersaturation results from the slow attainment of equilibrium with respect to double salts, results are in agreement.

COLLEGE PARK, MD. RECEIVED MAY 25, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Kinetics of the Quinhydrone Electrode Reaction[1]

BY ROBERT ROSENTHAL, ARTHUR E. LORCH AND LOUIS P. HAMMETT

Before dependable kinetic measurements of an electrode process may be made it is necessary, first, that the catalytic properties of the electrode surface be fairly reproducible and be constant during the interval of measurement, and, second, that all materials be of such purity as to avoid complicating side reactions. To date, these requirements have been satisfied only in the recent work on the hydrogen electrode process.[2-4] In the present work, we have studied the kinetics of another reversible electrode process, to wit, the quinone–hydroquinone system, employing apparatus designed to allow fulfilment of the above requirements. Early measurements on this system were made by Haber and Russ[5] but this phase of their very important pioneer work on electrode processes was of low precision, complicated by the appearance of a "reststrom," and was carried out at only one acidity in an 80% ethanol solution.

Experimental Method

Apparatus.—The reaction vessel, A, in Fig. 1 was constructed from a one-liter heavy-walled Pyrex bottle. Eight inner members of Bureau of Standards standard taper No. 15 ground glass joints were sealed in a ring close to the edge, and one inner No. 25 ground joint was sealed in the center of the top of the vessel. Through this latter runs a glass stirrer seated on a finely ground No. 15 joint, B, and water seal, C. This type of seating permits of stirring speeds in excess of 5000 r. p. m. without rattling or vibration, without ingress of air or overheating of the water seal. D is a thin strip of platinum foil of about three sq. cm. area, wrapped tightly around the glass tubing centering the stirrer. A fine platinum wire entering through a small hole (sealed over with Picein cement) in the stirrer adapter connects with this electrode.

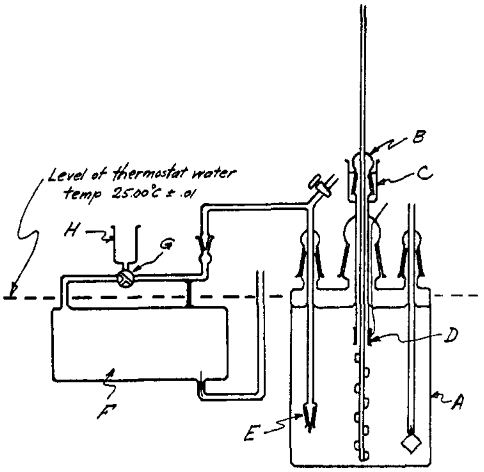


Fig. 1.

Through the eight peripheral ground joints were placed the following: (1) the salt bridge, provided with a ground-in plug, E, of the saturated calomel electrode, F (H is a reservoir of saturated potassium chloride solution used to flush the liquid junction at the beginning of each experiment); (2) a calibrated 10-ml. buret; (3) an addition tube (Fig. 2) for adding solids without ingress of air (a weighed amount of solid is placed in the tube, J, the stopcock, K, is closed and L and M are opened. Nitrogen gas which is bubbling through the solution is passed through these latter two stopcocks for about fifteen minutes, sweeping out J. Then L is closed and K opened, and the pressure of the nitrogen in the vessel forces solution up through N into J—then M is closed and L opened—

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[1] Dissertation submitted by Robert Rosenthal in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] (a) Bowden and Rideal, *Proc. Roy. Soc.* (London), **A120**, 59, 80 (1928); (b) Bowden, *Trans. Faraday Soc.*, **24**, 473 (1928); (c) Bowden, *Proc. Roy. Soc.* (London), **A126**, 107 (1929); (d) Bowden and O'Connor, *ibid.*, **A128**, 317 (1930).

[3] Hammett, THIS JOURNAL, **46**, 7 (1924).

[4] (a) Erdey-Gruz and Volmer, *Z. physik. Chem.*, **A150**, 203 (1930); (b) Erdey-Gruz and Wick, *ibid.*, **A162**, 53 (1932); (c) Volmer and Wick, *ibid.*, **A172**, 429 (1935); (d) Butler and Armstrong, *Proc. Roy. Soc.* (London), **A137**, 604 (1932).

[5] Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904).