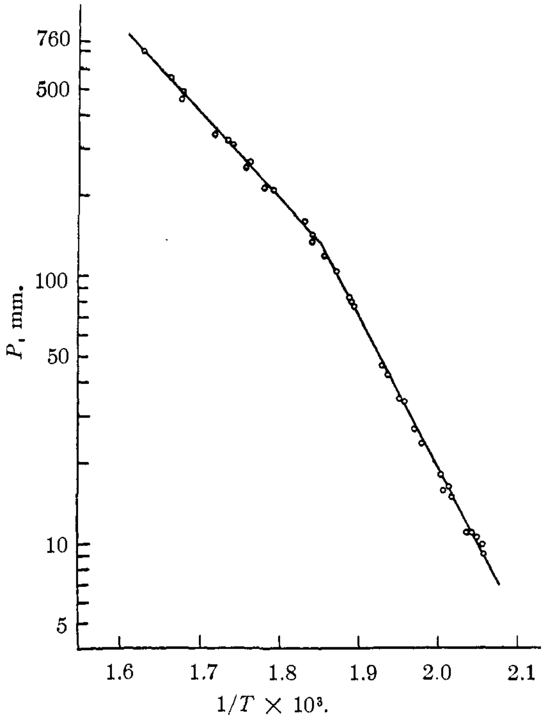

Fig. 1.—Vapor pressure of tantalum pentabromide.

temperatures is afforded by the study of the hydrogen reduction of tantalum pentabromide to tantalum tribromide at 700°.[4] Reduction at this temperature proceeds relatively slowly. In our many sublimations of tantalum pentabromide under various conditions formation of tantalum tribromide was never observed. Considering these observations and the conditions under which the pentabromide is prepared from the oxide, it seems unlikely that tantalum pentabromide dissociates appreciably below its boiling point.

Approximate vapor density calculations based on measurements where complete vaporization of the material occurred indicate that tantalum pentabromide is not appreciably associated in the vapor phase. This is to be expected from the electron diffraction results reported by Skinner and Sutton.[5]

Summary

The vapor pressure of tantalum pentabromide has been studied between 200 and 345°. The results may be expressed by the equations: solid (200–267°): $\log p_{\mathrm{mm.}} = -5650/T + 12.571$; liquid (267–345°): $\log p_{\mathrm{mm.}} = -3265/T + 8.171$.

[4] Young and Hastings, This Journal, **64**, 1710 (1942).

[5] Skinner and Sutton, *Trans. Faraday Soc.*, **36**, 668 (1940).

SEATTLE, WASHINGTON RECEIVED DECEMBER 6, 1948

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CO-OPERATION, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Exchange between Cobaltous Ion and Cobaltic Hydroxide in the Presence and Absence of Hydrogen Peroxide

BY D. B. BROUGHTON, R. L. WENTWORTH AND M. E. FARNSWORTH

It has been shown previously, by radioactive tracers, that no exchange takes place between manganous ion and colloidal manganese dioxide in aqueous solution.[1] However, when hydrogen peroxide is added, the catalytic decomposition of the peroxide is accompanied by rapid and complete exchange.[2] This has been attributed to cyclic oxidation and reduction of manganese by the peroxide.

The work described herein was done to determine whether hydrogen peroxide would induce a similar exchange between cobaltous ion and colloidal cobaltic hydroxide.

Experimental

Tests for exchange were made both between radioactive cobaltous ion and non-radioactive cobaltic hydroxide and between non-radioactive cobaltous ion and radioactive cobaltic hydroxide. This was done because of the possibility that the addition of hydrogen peroxide might change the distribution of cobalt between the cobaltous and cobaltic forms, and thus give a false indication of exchange on a single combination.

A sample of radioactive 5-year Co^{60}, prepared by bombardment in a cyclotron, was furnished by the M. I. T. Radioactivity Center. This was converted to a 0.138 *M* solution of cobaltous sulfate. The activity, as measured on a Geiger counter was about 45 counts per minute per mg. of cobalt. The scheme followed in determining exchange in the presence of peroxide is illustrated in Fig. 1.

Solutions 1, 2, 3 and 4 were made up, as shown, from cobalt sulfate, sodium hydroxide, and redistilled hydrogen peroxide, and the peroxide was allowed to decompose completely. This gave solutions containing part of the cobalt content as soluble divalent cobalt and the remainder as colloidal cobaltic hydroxide. The quantities of base were adjusted to give approximately equal distribution of cobalt between the two valence stages. (The relatively large quantity of base required was due to the presence of free sulfuric acid in the cobalt sulfate solutions.) The solutions were then filtered and the precipitates washed. P_1, F_2, F_3*, P_4 were analyzed for total cobalt by the method of Young and Hall,[3] to determine distribution between valences. The remaining filtrates and precipitates were then cross-mixed as shown in Fig. 1, so that one solution contained radioactive cobalt only in the soluble divalent form and the other only in the colloidal trivalent form; ten cc. of redistilled 38% peroxide was then added to each mixture and allowed to stand for twenty-four hours. During this period, the bulk of the peroxide decomposed, and the cobaltic hydroxide remained well dispersed. Traces of peroxide still remaining were then destroyed by treating with platinum foil. The solutions were filtered,

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[1] Polissar, This Journal, **58**, 1372 (1936).

[2] Broughton, Wentworth and Laing, *ibid.*, **69**, 741 (1947).

[3] Young and Hall, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 246 (1946).

and the filtrates and precipitates were analyzed for total cobalt and for radioactive cobalt by use of a Geiger counter.

Tests for exchange in the absence of peroxide were made by the same scheme, omitting the addition of peroxide to the cross-mixed solutions. The solutions were allowed to stand for twenty-four hours before filtration and analysis.

Results and Discussion

The results are given in Table I as total cobalt content and radioactivity of the solid and soluble phases, before and after the period in which exchange could have occurred. Material balances on total cobalt and total radioactivity close to within 5%. It is evident that very little exchange takes place in the twenty-four hour period and that hydrogen peroxide has no tendency to accelerate it. It is believed that the slight exchange indicated could be the result of adsorption of salts on the colloid and failure of the filter to remove the colloid completely.

TABLE I

EXCHANGE BETWEEN Co^{++} AND $Co(OH)_3$

Sample	Mg. Co	C. p. m./mg. Co	C. p. m./mg. Co for complete exchange
	A. In presence of H_2O_2		
F_1	41.6	0	..
P_3*	45.8	46.5	..
F_1'	42.2	3.1	24.4
P_3*'	44.7	45.3	24.4
F_4*	40.2	40.6	..
P_2	47.8	0	..
F_4*'	38.6	41.9	18.6
P_2'	43.6	2.3	18.6
	B. In absence of H_2O_2		
F_1	44.7	0	..
P_3*	44.7	49.0	..
F_1'	42.2	4.5	24.5
P_3*'	43.6	44.3	24.5
F_4*	40.2	46.2	..
P_2	43.1	0	..
F_4*'	41.0	38.8	22.4
P_2'	42.2	6.0	22.4

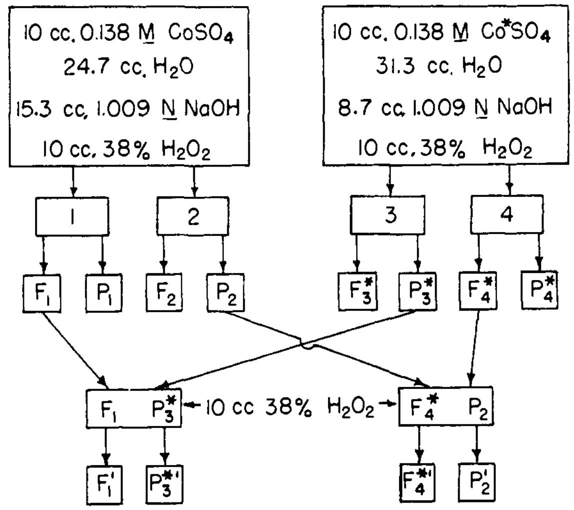

Fig. 1.

Acknowledgment.—The authors are indebted to the Naval Bureau of Ordnance for support of and permission to publish this work.

Summary

The extent of exchange between cobaltous ion and colloidal cobaltic hydroxide in water has been determined in both the presence and absence of hydrogen peroxide, by the use of a radioactive cobalt tracer. Within the accuracy of the methods, practically no exchange occurs in either case over a twenty-four-hour period.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Investigations of Galvanic Cells with Solid and Molten Electrolytes[1]

BY WALTER J. HAMER AND JOHN P. SCHRODT

Numerous investigations have been made of reversible cells with molten electrolytes.[2] For the most part these studies were made for the purpose of obtaining thermodynamic data on metallic solutions or molten salts and were conducted at temperatures at which all or part of the cell components were in the molten state. Few data, however, are available on cells of this type below the melting point of the electrolyte, on their characteristics in the inactive solid state, or on their discharge characteristics when there is a net flow of electric current.

Jacques,[3] Reed,[4] Baur[5] and Haber[6] and their

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[1] Presented at the Symposium on Galvanic Cells and Batteries before the Division of Physical and Inorganic Chemistry of the American Chemical Society, April 19, 1948.

[2] N. W. Taylor, THIS JOURNAL, **45**, 2865 (1923); E. J. Salstrom, T. J. Kew and T. M. Powell, *ibid.*, **58**, 1848 (1936); J. H. Hildebrand, "Solubility of Non-electrolytes," Reinhold Publ. Corp., 2nd ed., New York, N. Y., 1936, Chap. XI; C. Wagner and G. Engelhardt, *Z. physik. Chem.*, **159A**, 241 (1932); H. Seltz, *Trans. Electrochem. Soc.*, **77**, 219 (1940); J. A. Yanko, A. E. Drake and F. Hovorka, *ibid.*, **89**, 357 (1946).

[3] W. W. Jacques, *The Electrician*, **36**, 768 (1896).

[4] C. J. Reed, *J. Franklin Institute*, **142**, 1 (1896).

[5] E. Baur, *Z. Elektrochem.*, **16**, 300 (1910); E. Baur and H. Ehrenberg, *ibid.*, **18**, 1002 (1912); E. Baur, A. Petersen and G. Füllemann, *ibid.*, **22**, 409 (1916); E. Baur, W. D. Treadwell and G. Trümpler, *ibid.*, **27**, 199 (1921).

[6] F. Haber and L. Bruner, *Z. Elektrochem.*, **10**, 697 (1904); F. Haber and A. Moser, *ibid.*, **11**, 593 (1905); F. Haber, *Z. anorg. Chem.*, **51**, 245 (1906); F. Haber and G. W. A. Foster, *ibid.*, **51**, 289 (1906).