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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

Exchange Reactions of Uranium Ions in Solution

BY ELIZABETH RONA[1]

Exchange reactions with heavy isotopes have received increasing attention in recent years. The experiments presented here were undertaken to obtain information on the kinetics and mechanism of the exchange of uranium in the four and six oxidation states in hydrochloric acid solution. The exchange studied is represented by

$$\mathrm{U(IV)} + \mathrm{U^*(VI)} = \mathrm{U^*(IV)} + \mathrm{U(VI)}$$

where the ion with the asterisk is labelled with the artificial radioactive isotope U^{233}.

Recently Betts[2] reported experiments on the exchange of U(IV) and U(VI) ions in sulfuric acid solution. King[3] previously reported measurable exchange in three molar perchloric and six molar hydrochloric acid.

Experimental

Materials.—Uranyl chloride solution was prepared from purified uranyl nitrate hexahydrate. A weighed amount added (in the form of uranyl nitrate hexahydrate) was converted to uranyl chloride by repeated evaporation to dryness with hydrochloric acid. A stock solution of 0.300 molar uranyl chloride in 0.140 molar hydrochloric acid was prepared, and this solution was diluted to the proper concentration of uranyl chloride for each experiment with 0.140 molar hydrochloric acid. Spectroscopic analysis showed that the impurities were less than 0.1%.

The uranium tetrachloride was a resublimed product. Chemical analysis indicated a ratio U:Cl of 1 to 3.94. It was dissolved in oxygen-free hydrochloric acid of a concentration which by trial gave the desired *p*H at a time two to five min. after mixing the uranium tetrachloride solution with an equal volume of stock uranyl chloride solution. For example, 0.136 to 0.139 molar hydrochloric acid, depending on the concentration of the U(IV) and U(VI) ions, was used to obtain reaction mixtures of *p*H 0.85. The uranium tetrachloride solution was prepared immediately before the beginning of each experiment to avoid oxidation.

The alpha emitter U^{233} was used as a tracer,[4] since its specific activity is high compared to that of U^{235}, and a correction can be applied for the U^{238} activity. The U^{233} was kindly supplied by F. T. Hagemann.

Experiments.—Equal volumes of uranium tetrachloride and uranyl chloride solutions were mixed in a reaction vessel which had an inlet and outlet for nitrogen. The vessel was immersed in a water-bath, the temperature of which could be maintained within 0.05°. The exchange mixture was kept in an atmosphere of oxygen-free nitrogen, saturated with water vapor, throughout the experiments. The time of mixing was taken as the starting time of the experiment. Samples for analysis were forced by nitrogen pressure through a side arm into calibrated centrifuge cones at convenient time intervals. The reaction was stopped by chilling the sample in an ice-bath, and the sample was then analyzed.

For the interpretation of the results it was important to know whether U(IV) could be oxidized to U(VI) under the standard conditions of the experiments. Blanks were run with uranium tetrachloride without the addition of uranyl chloride. A hydrochloric acid solution containing U^{233} and a few mg. of uranyl chloride was reduced to the plus four oxidation state with a mercury cathode, in an atmosphere of oxygen-free nitrogen. This was then added to the uranium tetrachloride solution of the required concentration. Samples were taken at convenient time intervals, and handled in the same manner as those of the mixture. No measurable oxidation was detected in several days.

Of the main factors which might influence the velocity of exchange, those of U(IV) and U(VI) concentrations, hydrogen ion concentration, temperature, concentration of an added inert salt, chloride ion concentration, and light were investigated. The concentrations of the U(IV) and U(VI) ions were systematically varied in the range of 0.02 to 0.15 molar. The effect of hydrogen ion concentration was studied in a *p*H range of 0.85 to 1.6. The narrow range was imposed by the fact that below 0.85 the exchange is very slow, and at a *p*H higher than 1.6 hydrolysis becomes troublesome. The *p*H of the reaction mixture was measured both at the beginning and at the end of each experiment with a Beckman *p*H meter using a glass electrode. The hydrogen ion concentration became constant two or three min. after mixing the U(IV) and U(VI) ions, because the actual concentrations of the two ions remain

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[1] Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee.

[2] H. H. Betts, *Can. J. Research*, **26**, 702 (1948).

[3] E. L. King, Manhattan District Declassified Document MDDC-813 (1947).

[4] G. T. Seaborg, J. F. Gofman and R. W. Stoughton, *Phys. Rev.*, **71**, 378 (1947).

essentially constant during the experiment, and the slight hydrolysis sets in quickly after mixing. The effect of an inert salt on the exchange was determined by adding varying amounts of sodium perchlorate to the reaction mixture, and that of chloride ions by adding sodium chloride. Finally, the rate was observed under light and dark conditions.

Separation of U(IV) and U(VI) Ions.—Several methods of separation of U(IV) and U(VI) ions were tested. The method finally adopted was precipitation of U(IV) in hydrofluoric acid as the tetrafluoride. The precipitation is instantaneous and quantitative, and all the U(VI) remains in the supernatant solution. No induced exchange was observed. After separation, the precipitate was washed repeatedly with dilute hydrofluoric acid, and dissolved in a mixture of hydrogen peroxide and hydrochloric acid. The total activity and that of the dissolved U(IV) precipitate were determined by evaporating an aliquot of each on a platinum disc and measuring the alpha activity in an air chamber, attached to a counting circuit.[5] Three aliquots were counted for each sample.

All the experiments were carried out in triplicate. The limit of error for an experiment, including the analytical error, timing, pipetting and counting the samples, was estimated to be about ±10%.

Results

Treatment of the Results.—In treating the results it is convenient to use the fact that the rate of appearance of the tracer in the plus four state must be first order with respect to the concentration of the tracer.[6] Let a be the total concentration of U(IV), b the total concentration of U(VI), x the concentration of the tracer in the U(IV) form, and y the concentration of the tracer in the U(VI) form. The rate of the exchange reaction, R, is a function of the concentrations a and b and is a constant in a single experiment. The rate of appearance of x can be expressed by the following differential equation

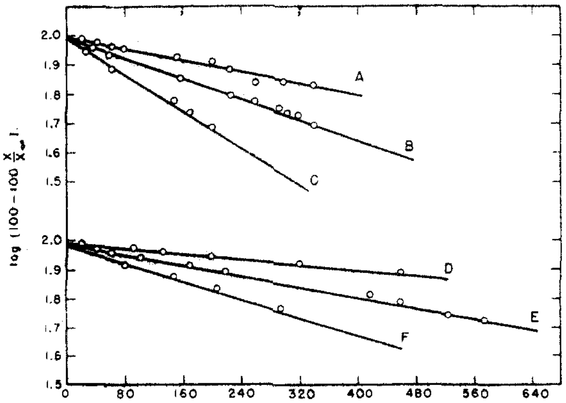

Fig. 1.—Dependence of exchange rate on uranium concentration at a pH of 0.85 and 25.00°: A, 0.0300 M UCl_4–0.0274 M UO_2Cl_2; B, 0.0400 M UCl_4–0.0274 M UO_2Cl_2; C, 0.064 M UCl_4–0.0274 M UO_2Cl_2; D, 0.0250 M UCl_4–0.0240 M UO_2Cl_2; E, 0.0250 M UCl_4–0.0750 M UO_2Cl_2; F, 0.0250 M UCl_4–0.1500 M UO_2Cl_2.

$$\frac{dx}{dt} = R\left(\frac{y}{b} - \frac{x}{a}\right) \tag{1}$$

At zero time, $x = 0$; at infinite time $x = x_\infty$ and $y = y_\infty$; also, $ay_\infty = bx_\infty$ and $x + y = x_\infty + y_\infty$. Substituting these values and integrating equation (1) the following equation is obtained

$$-\ln\left(1 - \frac{x}{x_\infty}\right) = \frac{a + b}{ab} Rt \tag{2}$$

x/x_∞ can easily be shown to be equal to the expression

$$\frac{x}{x_\infty} = \frac{\text{U(IV) activity}}{\text{total activity}} \frac{a + b}{a} \tag{3}$$

log (100 − 100 $x/x\infty$) is plotted against time, and R is obtained from the slope, K', by the relation

$$R = -K' \, 2.303 \, ab/(a + b) \tag{4}$$

Effect of Uranium Concentration.—The results of experiments in which the uranium concentrations were varied at constant pH and temperature are shown in Fig. 1 and Table I.

TABLE I

DEPENDENCE OF RATE OF EXCHANGE ON CONCENTRATIONS AT pH 0.85 AND TEMP. 25.00°

Concentration in moles/liter U(IV)	UO_2^{+2}	R (moles/liter/min. × 10^6)
0.030	0.0274	7.45
.040	.0274	13.35
.064	.0274	33.80
.025	.024	2.87
.025	.075	9.54
.025	.150	18.00

It can be seen from Fig. 1 that the tracer exchange follows the first order law, given in equation (2). In Fig. 2 log R is plotted against the logarithm of the varied concentration of one ionic species, keeping the other concentration constant. From curve A of Fig. 2 it can be seen that the reaction is second order with respect to the U(IV) concentration, and from B that it is first order with respect to the U(VI) concentration.

Hydrogen Ion Concentration.—In Fig. 3 log (100 − $100x/x_\infty$) is plotted against time for experiments carried out in the range of pH 0.85 to 1.6 at the constant temperature of 25.00° and at a constant uranium tetrachloride concentration of 0.025 molar and a constant uranyl chloride concentration of 0.0274 molar. In Fig. 4 the logarithm of $-K'$ from these curves is plotted against pH. From this plot it can be seen that the rate of reaction has a minus third order dependence on hydrogen ion concentration.

Temperature.—In Fig. 5 log (100 − 100·x/x_∞) is plotted against time at a pH of 0.85 and a constant concentration of uranium tetrachloride of 0.025 molar and of uranyl chloride of 0.0275 molar. The logarithm of $-K'$ against the reciprocal temperature is plotted in Fig. 6. The rate of exchange is markedly increased by temperature. The apparent energy of activation,

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[5] A. H. Jaffey, T. P. Kohman and J. Crawford, Manual on the Measurement of Radioactivity, Manhattan District Declassified Document MDDC-388 (1944).

[6] (a) H. A. C. McKay, *Nature*, **142**, 997 (1938); (b) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

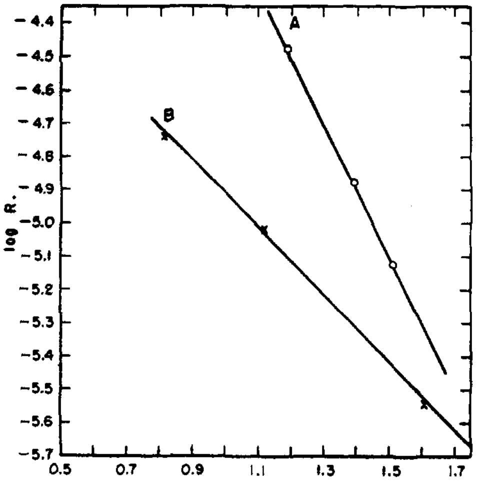


Fig. 2.—Determination of the order of reaction by varying the concentration of the reactants, at a *p*H of 0.85 and 25.00°: A, UCl_4 concentration varied, UO_2Cl_2 concentration 0.0274 *M;* B, UCl_4 concentration 0.025, UO_2Cl_2 concentration varied.

calculated from the slope of the straight line, is equal to 33,400 ± 800 cal. per mole.

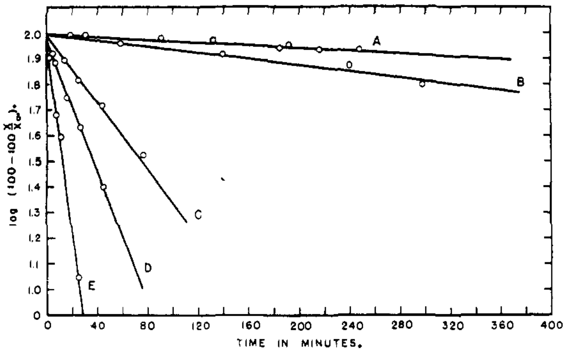


Fig. 3.—Dependence on hydrogen ion concentration at 25.00°: 0.025 *M* UCl_4-0.0274 *M* UO_2Cl_2 at a *p*H of: A, 0.85; B, 0.96; C, 1.30; D, 1.50; E, 1.60.

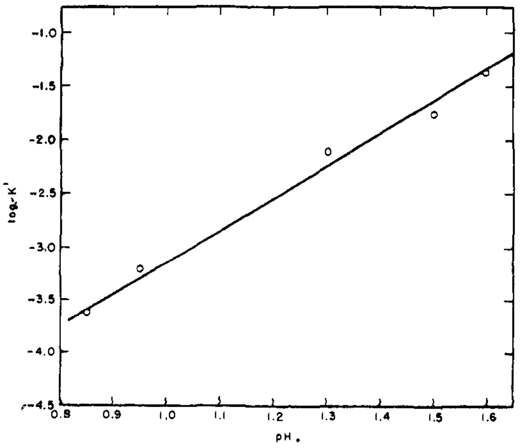


Fig. 4.—Dependence on hydrogen ion concentration at 25.00° of 0.025 *M* UCl_4-0.0274 *M* UO_2Cl_2.

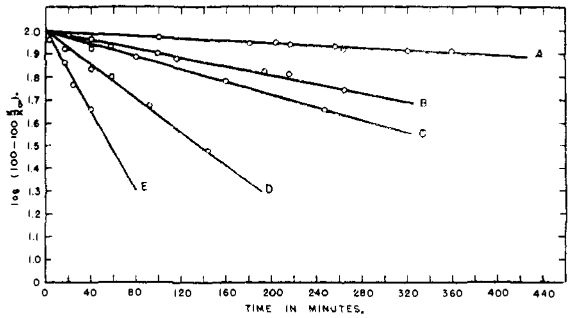


Fig. 5.—Dependence on temperature at *p*H 0.85, 0.025 *M* UCl_4-0.0274 *M* UO_2Cl_2: A, 25.00°; B, 30.4°; C, 34.1°; D, 38.9°; E, 43.5°.

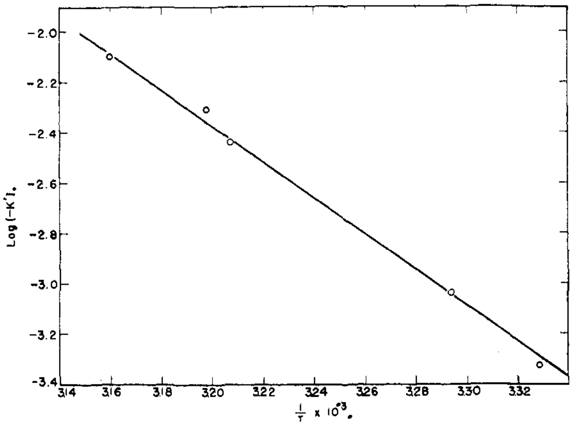


Fig. 6.—Dependence on temperature at a *p*H of 0.85, 0.025 *M* UCl_4 and 0.0274 *M* UO_2Cl_2.

Salt Effect.—To study the effect of an added inert salt on the velocity of exchange, various amounts of sodium perchlorate up to a concentration of 0.943 molar were added to a mixture of U(IV) and U(VI) chlorides. In Fig. 7A two typical experiments are represented in which the velocity of exchange was measured in a mixture of 0.0125 molar uranium tetrachloride and 0.0125 molar uranyl chloride in hydrochloric acid solution at a *p*H of 1.28, one without sodium perchlorate and one with the addition of sodium perchlorate to a concentration of 0.943 molar. No appreciable salt effect was observed in any of the experiments.

Effect of Chloride Ion.—In the experiments which were carried out for the purpose of determining the order of the reaction with respect to the U(IV) and U(VI) ions, the concentrations of the chloride ions were naturally varied proportionally. To check whether an increase of chloride ion concentration influences the velocity of exchange, two experiments were carried out: one with 0.025 molar uranium tetrachloride and 0.0274 molar uranyl chloride in 0.14 molar hydrochloric acid and one with the same mixture plus sodium chloride at a concentration of 1.32 molar. From Fig. 7B it can be seen that the addition of chloride ions did not influence the velocity of exchange.

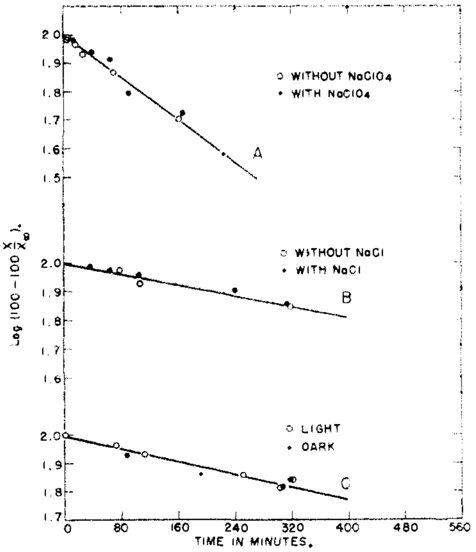


Fig. 7.—Dependence of exchange rate at 25° on inert salt, chloride ion concentration and light: A, 0.0125 *M* UCl_4, 0.0125 *M* UO_2Cl_2, *p*H 1.28, with and without 0.943 *M* $NaClO_4$; B, 0.025 *M* UCl_4, 0.0274 *M* UO_2Cl_2, *p*H 0.85, with and without 1.32 *M* NaCl; C, 0.025 *M* UCl_4, 0.0274 *M* UO_2Cl_2, *p*H 0.85, under light and dark conditions.

Light.—In Fig. 7C two sets of experiments are represented, one under "light" and the other under "dark" conditions. The experiments under "light" conditions were carried out by illuminating the mixture with a 100-watt tungsten lamp at a distance of 100 cm. The "dark" condition was established by carrying out the exchange reaction in a dark room, in a vessel painted black. It can be seen that the light had no effect on the rate.[7]

Discussion of Mechanism

The experimental data show that the rate of exchange of U(IV) and U(VI) ions is of first order with respect to the U(VI) concentration, second order with respect to the U(IV) concentration, and minus third order with respect to the hydrogen ion concentration. To present a mechanism for this complicated reaction a knowledge of the ionic forms of the U(IV) and U(VI) ions is necessary. There is strong experimental evidence that U(VI) is present in the form[8,9,10] of UO_2^{+2} in moderate acid concentration. The principal ions of tetravalent uranium are U^{+4} and UOH^{+3} in reversible rapid equilibrium with each other, and the equilibrium constant, K_h, of the reaction

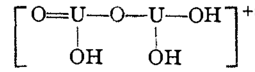
$$U^{+4} + H_2O \rightleftarrows UOH^{+3} + H^+ \qquad (5)$$

has been evaluated at various ionic strengths.[11] The analytically determined U(IV) concentration is the sum of the concentrations of these two ions. Actually all these ions are aquo complexes with an unknown number of water molecules.

In the U(IV)-U(VI) exchange system, it is reasonable to assume that the oxygenated ion of the U(IV) will react more readily with the UO^{+2} ion, and that one step involves an oxygen bridge between the two ions. To account for the experimental facts the following mechanism is proposed.

$$UOH^{+3} + UO_2^{+2} + 2H_2O \rightleftarrows Y^{+3} + 2H^+, \quad \text{rapid reversible} \qquad (6)$$

Here Y^{+3} is a postulated intermediate ion, which may have the form



$$\left[\begin{array}{c} O{=}\underset{\displaystyle OH}{\underset{|}{U}}{-}O{-}\underset{\displaystyle OH}{\underset{|}{U}}{-}OH \end{array}\right]^{+3}$$

The equilibrium constant for reaction (6) is K_1.

$$Y^{+3} + UOH^{+3} = Z^{+6}_{act}, \text{ rate determining} \qquad (7)$$

Z^{+6}_{act} is the activated complex in the theory of absolute reaction rates which breaks down into the final products UOH^{+3} and UO_2^{+2}. Further, the reaction rate, *V*, is given by

$$V = k[Y^{+3}][UOH^{+3}] \qquad (8)$$

Solving the equilibrium expression for reaction (6) for $[Y^{+3}]$ and substituting in (8)

$$V = kK_1[UOH^{+3}]^2[UO_2^{+2}]/[H^+]^2 \qquad (9)$$

Solving the equilibrium expression for reaction (5) for $[UOH^{+3}]$ in terms of $[U(IV)] = [U^{+4}] + [UOH^{+3}]$ and substituting in (9)

$$V = kK_1 \frac{[U(IV)]^2[UO_2^{+2}]}{\left(\frac{[H^+]}{K_h} + 1\right)^2 [H^+]^2} \qquad (10)$$

In these expressions the activity coefficients are omitted because of the difficulty of evaluating them in aqueous solutions of strong electrolytes in the range where the Debye-Hückel theory does not apply.

The rate according to equation (10) is second order with respect to U(IV) and first order with respect to UO_2^{+2}, in agreement with the experiments. With respect to hydrogen ion it is minus fourth order at high acidities and minus second order at low acidities. By using for K_h the value of 0.034 from Kraus and Nelson's data[11] at the ionic strength of the experiments on *p*H dependence it is found that, over the *p*H range of 0.85 to 1.60 which was covered in the experiments, $\Delta \log V / \Delta \log [H^+] = -3.26$. This is in good agreement with the observed value of -3.0.

This mechanism is open to the objection that there probably should be a large salt effect because of the highly charged ions in the rate

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(7) It was observed recently by H. G. Heal and J. G. N. Thomas (*Trans. Faraday Soc.*, **45**, 11 (1949)) that there is no Becquerel effect in a mixture of U(IV) and U(VI) ions in hydrochloric acid solution, whereas there is a marked light sensitivity in sulfuric acid at a *p*H of one or higher.

(8) F. Sutton, Canadian Research Council Report No. 325 (1947).

(9) D. A. MacInnes and L. C. Longsworth, Manhattan District Declassified Document, MDDC-911 (1942).

(10) H. W. Crandall, *J. Chem. Phys.*, **17**, 602 (1949).

(11) K. A. Kraus and F. Nelson, Oak Ridge National Laboratory Report ORNL-496 (1950).

determining step, equation (7), whereas experimentally no salt effect was observed. On the other hand, it is the only mechanism which has been found to explain the order of the reaction with respect to the various reactants.

Acknowledgment.—The author is indebted for helpful discussions to Dr. J. J. Katz, Dr. D. W. Osborne and Dr. Martin Kilpatrick, and to Dr. Bruce Longtin for suggestions for the mechanism.

Summary

Exchange reactions between U(IV) and U(VI) in hydrochloric acid solutions have been studied. It was found that the reaction is of the first order with respect to the U(VI), second order with respect to the U(IV), and minus third order with respect to the hydrogen ion concentration. The rates of exchange did not change with added inert salt, with chloride ion concentration, nor with illumination. The apparent heat of activation was found to be 33,400 ± 800 cal. per mole.

A mechanism is proposed for the exchange.

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[CONTRIBUTION FROM INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

Studies of Copper Surfaces by Low Temperature Adsorption Isotherms

BY T. N. RHODIN, JR.

Introduction

Much of the research that has been done in the past on the corrosion of metals and on the reactions between gases and metals has been handicapped by a lack of knowledge of the surface structure in general and of the true surface area in particular. It is now recognized that the physical adsorption of gases near their boiling points provides a method for determining true surface area under certain circumstances using the Brunauer–Emmett–Teller interpretation.[1] The absolute method of Harkins and Jura[2] for the determination of surface areas makes it possible to evaluate the effective cross-sectional area of some adsorbate molecules without making questionable assumptions.

The methods using gases such as nitrogen near their boiling points as adsorbates are ordinarily capable of giving a reproducible surface area if the sample has an area of one square meter and a bulk volume of only a few cubic centimeters. When the particles are large and the adsorptions are small the common technique of following the adsorption by measuring the change in pressure of the gas at constant volume in the presence of the adsorbent becomes inaccurate. This difficulty can be avoided by using a gas having a low vapor pressure at the temperature of the run. Using ethylene, for example, at 78.1°K. and very sensitive pressure gages, the sensitivity of the method can be extended to permit the measuring of surfaces as low as one hundred square centimeters.[3] It is evident that this method is still not sufficiently sensitive for the surface chemistry study of metal specimens of small enough area to be conveniently prepared. Very sensitive beam microbalances have sufficient sensitivity to measure adsorptions as small as one ten thousandth of a cubic centimeter (STP) but their use in adsorption studies has been relatively limited.[4] The main sources of error in their application have been the large buoyancy corrections required and the presence of thermal eddy currents which obscure the rest-point determination. It is the purpose of this paper to show how surfaces of copper samples, ten square centimeters in area, subject to various oxidation–reduction treatments, can be studied by microbalance measurements of gas adsorptions at low temperatures.

Procedure

Technique.—The system used for measuring the adsorption is schematically indicated in Fig. 1. Gas pressures were measured over the range 10^{-6} to 760 mm. with the usual combination of McLeod gage, ionization gage, and mercury manometer. The gages had been cross-calibrated. The tank nitrogen and tank argon were passed over copper at 500°, a phosphorus pentoxide drying column, a liquid nitrogen trap and a cotton filter to remove oxygen and any condensable gases. The tank oxygen and tank hydrogen were dried in the same system by-passing the copper furnace. The metal sample, hanging in place at one end of the microbalance beam, was outgassed at 400° to a vacuum of 10^{-7} mm. in the presence of a 50/50 barium–aluminum getter. The sample was then cooled to a low temperature. Introduction of spurious vapors to the sample after cooling was minimized by separating the microbalance and getter from the rest of the system by mercury cut-offs and a liquid nitrogen trap. The microbalance case was outgassed at 300° prior to a run. It was also suitably shock-mounted, electrically grounded and thermostated at 40 ± 0.02°.

The vacuum microbalance developed by Gulbransen[5] and modified by the author is suited to the study of surface effect involving small weight changes. Its high sensitivity and reasonable stability are its most important merits. It is also important that it can be adequately baked out and vacuum up to 10^{-7} mm. may be obtained with it using suitable getter material. The operation of the balance is presented elsewhere.[5] It was possible to observe

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[1] P. H. Emmett, S. J. Brunauer and E. Teller, THIS JOURNAL, **60**, 309 (1938); P. H. Emmett, "Advances in Catalysis," Academic Press, New York, N. Y., 1948, pp. 65.

[2] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1366 (1944); **66**, 1362 (1944).

[3] Wooten and Brown, *ibid.*, **65**, 113 (1943).

[4] H. M. Barrett, A. W. Birnie and M. J. Cohen, *ibid.*, **62**, 2839 (1940).

[5] E. A. Gulbransen, *Rec. Sci. Inst.*, **15**, 201 (1944).