From studies of the dependence of rate of adsorption (after titration) on *p*H and salt concentration it was established that a decrease in hydrogen ion concentration from *p*H 7.5 to 8.0 or 8.5 increased the rate while an increase in ammonium chloride concentration from 3.8×10^{-3} to 3.0×10^{-1} *N* increased the rate.

A rate equation has been derived postulating a displacement of adsorbed monovalent cations by divalent cations. The experimental data on rate of adsorption of barium ions from dilute solution (3×10^{-10} gram atom per liter) were found to fit this equation.

RECEIVED MAY 22, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF GODFREY L. CABOT, INC.]

The Adsorption of Helium on Carbon Black at Liquid Helium Temperatures[1]

BY W. D. SCHAEFFER, W. R. SMITH AND C. B. WENDELL

Previous investigators[2,3,4,5] have studied the adsorption of helium on various adsorbents of poorly defined total surface area. In one investigation[4] the heat of adsorption of helium on charcoal (Carbotax) was calculated from isotherms at liquid and solid hydrogen temperatures. Values ranging from 416 to 127 calories were reported. van Dingenen[3] reported heats of 93 to 52 cal./mole calculated from the isotherms of helium on glass at and below the temperature of liquid helium. Stout and Giauque[2b] report values of 131 to 148 calories for the heat of adsorption of helium on $NiSO_4 \cdot 7H_2O$ at 4.23°K. These values were computed from the Sackur–Tetrode equation, assuming zero entropy for the adsorbed helium. Keesom and Schweers[2a] measured the quantity of helium adsorbed in the temperature range, 4 to 1°K., on layers of hydrogen, neon, nitrogen and oxygen all solidified on glass. Isosteric heats of adsorption varied from 100 to 29 cal./mole, and led to the conclusion of multimolecular adsorption since the adsorption energy rapidly decreased at adsorbate concentrations representative of completed layers.

The Brunauer, Emmett and Teller procedure[6] for determining surface area from low temperature adsorption isotherms has been widely used in determining the area of commercial carbon blacks,[7,8,9] and has been particularly successful when the isotherms were determined at 78°K. with nitrogen as the adsorbate. The question as to the nature of the isotherm and the atomic area which might be revealed when helium was used as the adsorbate at 4.2°K. has interested us for some time. In addition to evaluating the B.E.T. expression at 4.2°K., adsorption studies with helium on carbon black of well defined area provide a simple system for observing the vigor of the van der Waals association between a simple atom and an essentially graphitic surface.[10]

Since a supply of liquid helium has recently become available in close proximity to our laboratory we have been able to determine the helium isotherms on two samples of commercial carbon black, Spheron 6 and Spheron C, at 4.2°K.

Experimental

By arrangement with Arthur D. Little, Inc., of Cambridge, Massachusetts, a supply of 2 to 3 liters of liquid helium per day was assured. The helium was liquefied in the Little laboratories in the Collins cryostat.[11] A system of double Dewar flasks, the outer containing liquid nitrogen, served to transport the liquid helium, and also provided the bath for the adsorption system. The inner helium Dewar flask of 1100 cc. capacity was constructed of unsilvered Pyrex and was 71 mm. in diameter and 267 mm. deep. The neck was constricted to 33 mm.; 250 mm. of 15-mm. Pyrex tubing ending in a well-ground stopcock was sealed to the neck of the flask. There was, of course, no need to evacuate the interspace of this Dewar flask since when the stopcock was closed and the flask filled with liquid helium the air in the interspace rapidly solidified, providing an excellent vacuum. This arrangement also facilitates the precooling of the entire system with liquid nitrogen prior to filling with liquid helium. The "helium Dewar" was immersed to the neck in liquid nitrogen contained in a tall 9-liter stainless steel Dewar flask. The inner flask, after cooling to −195° C., was then filled to the neck with liquid helium by siphoning directly from the Collins cryostat, and the mouth of the flask closed with a plug of glass wool. It was possible to transport the helium in this system by car to the authors' laboratory, a matter of five miles, without appreciable loss of liquid helium.

The familiar type of constant pressure adsorption apparatus used in surface area determinations was employed.[9] The adsorption cell was only 1 cc. in volume in order to keep the "dead" space to a minimum. To insure rapid cooling with a minimum loss of liquid helium the walls of the adsorption cell were made as thin as possible. As shown in Fig. 1, the cell was joined to the adsorption line through a Pyrex capillary about 1 mm. in diameter. The cell was immersed some 35 cm. into the helium bath. During a run the level of the liquid helium dropped 2 to 3 cm. Since the liquid helium in the bath could not be replenished by any of the usual siphon arrangements, the variations in temperature of the exposed capillary dead

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[1] Presented before the Division of Colloid Chemistry, Chicago Meeting, American Chemical Society, April 19, 1948.

[2] (a) W. H. Keesom and J. Schweers, *Physica*, **8**, 1032 (1941); (b) J. W. Stout and W. F. Giauque, THIS JOURNAL, **60**, 393 (1938).

[3] W. van Dingenen, *Physica*, **6**, 353 (1939).

[4] A. van Itterbeek and W. van Dingenen, *ibid.*, **5**, 529 (1938).

[5] A. van Itterbeek, W. van Dingenen and I. Borghs, *Nature*, **144**, 249 (1939).

[6] S. Brunauer and P. H. Emmett, THIS JOURNAL, **59**, 2682 (1937).

[7] R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, *ibid.*, **69**, 95 (1947).

[8] R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, *ibid.*, **69**, 2294 (1947).

[9] W. R. Smith, F. S. Thornhill and R. I. Bray, *Ind. Eng. Chem.*, **35**, 1303 (1941).

[10] J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

[11] Anonymous, *Chem. Eng. News*, **25**, 3370, 3450 (1947).

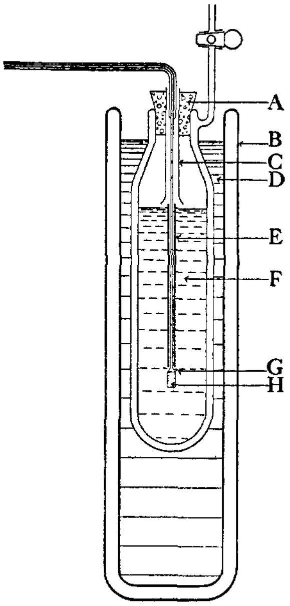

Fig. 1.—Helium bath and adsorption cell: A, cork stopper; B, stainless-steel Dewar flask; C, flared glass tube for exciting gases; D, liquid nitrogen; E, copper tube; F, liquid helium; G, stem for filling adsorbent cell; H, adsorbent.

space were reduced by encasing the capillary stem in a copper sheath which extended well below the level of the liquid helium. A section of Pyrex tubing with one end belled out as shown served to guide the helium vapors boiling off the bath around the upper portion of the stem.

Helium at liquid nitrogen temperatures was used to determine the dead space for the nitrogen isotherms. The volume of helium in the dead space at 4.2°K. was calculated from *PVT* relations.

Spheron 6, a medium processing rubber grade of channel black, and Spheron C, a much smaller particle size rubber black, were used as adsorbents. Spheron 6 had a surface area as determined by nitrogen adsorption of 113 sq. m./g. Its mean diameter, as observed under the electron microscope, is 285 Å. Spheron C had an area of 227 sq.m./g. and a mean diameter of 190 Å., 0.2-g. samples of each black were employed. The blacks were introduced and removed from the Pyrex adsorption cell through the small stem G which could be sealed and unsealed without causing observable changes in the dead space of the system. Prepurified grades of nitrogen and helium obtained from the Matheson Company were used without further treatment, while the helium was passed through degassed, evacuated charcoal at 78°K. prior to use.

The carbon black samples were degassed at 200 ± 10°C. for two hours. Nitrogen surface areas were first obtained at 78°K. The nitrogen was then pumped off, and the sample degassed for another hour at 200°C. After precooling with liquid nitrogen, the liquid helium bath, as shown in Fig. 1 was slowly lifted over the cell until the latter was immersed some 35 cm. in the bath. The system was then allowed to equilibrate for approximately fifteen minutes before starting the adsorption. Over the entire pressure range the adsorption was characterized by rapid approach to equilibrium. Ten minutes was sufficient to attain this condition in all instances. Pressures lower than 10 mm. must be viewed with reservations due to the possibility of thermal transpiration[12] at the gas outlet inducing non-equilibrium pressures between adsorbent and manometer.

Discussion

Figure 2 presents the helium isotherms at 4.2°K. on Spheron 6 and Spheron C. The isotherms are of the sigmoid type normally encountered with non-polar gases on carbon black.[13,9] The adsorption fits the simple B.E.T. expression

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\, x \qquad (1)$$

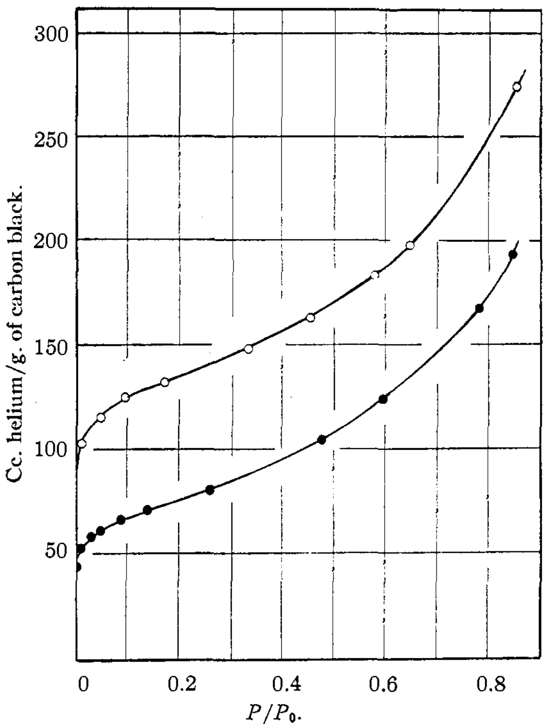

Fig. 2.—Adsorption isotherms of helium at 4.2°K. on ○, Spheron 6 and ●, Spheron C.

in which V_m is the volume of adsorbate (S.T.P.) required to form a monolayer, V is the volume of gas (S.T.P.) adsorbed at the relative pressure, x, and C is a constant peculiar to the adsorbent, adsorbate and temperature employed. The B.E.T. plots are illustrated in Fig. 3. At relative pressures larger than 0.25 there is some deviation from linearity as is generally encountered when the simple B.E.T. expression is employed. The V_m and c values obtained by least squares treatment of these data are summarized in Table I.

TABLE I

Adsorbent	Adsorbate	V_m, cc. at NTP	c	$E_1 - E_L$, cal.	$\frac{V_m(\text{He})}{V_m(\text{N}_2)}$	Area, sq. m./g.
Spheron 6	Helium	62.1	310	20.9	2.4	257.6[a]
	Nitrogen	25.9	187	352		113.0[b]
Spheron C	Helium	113.9	820	24.4	2.2	472.7
	Nitrogen	52.1	853	454		227.8

[a] Assuming cross section of 15.4 Å.^{2} calculated from density of liquid. [b] Assuming cross section of 16.2 Å.^{2} calculated from density of liquid.

The generally accepted cross sectional area of the nitrogen molecule is 16.2 Å.^{2} as calculated from the equation[14]

$$A = 4(0.866)\left(\frac{M}{4\sqrt{2}\,\text{N}aD_L}\right)^{2/3}$$

in which A is the average area occupied by each adsorbed molecule, M is the molecular weight of

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(12) E. F. Burton, H. G. Smith and J. O. Wilhelm, "Phenomena at the Temperature of Liquid Helium," Am. Chem. Soc. Monograph No. 83, Reinhold Publishing Corp., New York, N. Y., 1940.

(13) J. Holmes and P. H. Emmett, *J. Phys. Colloid Chem.*, **51**, 1262 (1947).

(14) P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 1558 (1937).

the gas, D_L is the density of the normal liquid or solid, N_a is Avogadro's number, and the molecules are assumed to be hexagonally close-packed in a face-centered cubic lattice. The cross sectional area of the helium atom, as computed from its liquid density of 0.125 g./ml.[15] is 15.4 Å.^{2}; consequently, the volume of helium required to fill a monolayer on a non-porous carbon black should be only slightly larger than that for nitrogen. Experimentally, however, the expectation of similar V_m's for the adsorption of nitrogen and helium is not realized.

Two obvious explanations of the anomalous V_m's may be offered. Either the carbon blacks have a large percentage of pores which accommodate the helium atoms, but are too small to admit the nitrogen molecules, or the cross sectional area of the helium atom as calculated from the liquid density is much larger than the space actually occupied by an adsorbed helium atom. The first interpretation appears rather improbable in view of the substantial agreement of the ratios of helium to nitrogen V_m's on Spheron 6 and Spheron C; the possibility of similar pore size as well as pore size distributions for two carbon blacks of markedly different average diameters being extremely remote. Moreover, electron micrographs and nitrogen adsorption at high relative pressures[13] indicate negligible porosity. It appears more logical to assume that the greater volume of helium adsorbed is due to a cross sectional area much smaller than that computed from the liquid helium density. If the cross sectional area of the hexagonally-packed helium atom is modified to yield surface areas of the two carbon blacks in agreement with those obtained with nitrogen, values of 6.77 and 7.43 Å.^{2} are obtained. These areas correspond to interatomic distances of 2.80 Å. and 2.92 Å. X-Ray diffraction patterns of solid helium[16] at 1.45°K. and 37 atmospheres indicate a close-packed hexagonal structure with interatomic distances of 3.07 Å. in the (100) plane and 2.75 Å. in the (101) plane, and a density of 0.207 g./c. Thus, the interatomic distance of 2.80 Å. calculated above for the adsorbed helium is nearly identical to that for solid helium.

The possibility of penetration of helium atoms of 1.40 Å. radius between the planes of the quasi-graphitic crystallites constituting the carbon black particles was considered. A calculation similar to that of Barrer's[17] indicates an energy barrier of only 34 cal./mole to the migration of a helium atom across the graphite hexagon, and slightly less than 68 cal./mole for penetration between the graphite planes. Although the heats of adsorption of helium at low surface coverage are unquestionably greater than 68 cal./mole, the work of Rossman and Smith[18] demonstrates that even at 25° C. no significant penetration of helium into graphite lattices could be detected. If, on the other hand, adsorbed helium at 4.2°K. were to partake to a certain degree the energy and physical characteristics of helium II, the enhanced helium adsorption on carbon black could probably be attributed to diffusion into the graphite lattice. The phase diagram does not permit the presence of He II at 4.2°K., and until possible phase changes of helium in the adsorbed state have been investigated this consideration remains purely speculative.

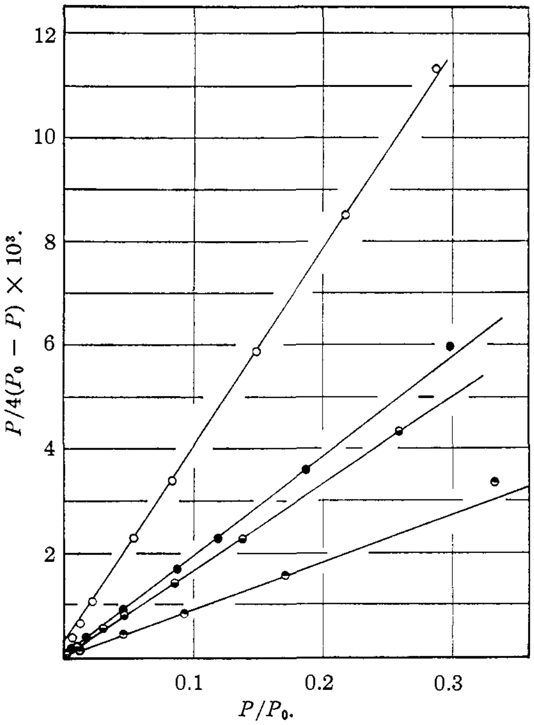

Fig. 3.—B. E. T. plots of helium and nitrogen: ○, nitrogen on Spheron 6 at 78°; ●, nitrogen on Spheron C at 78°; ◒, helium on Spheron 6 at 4.2°; ◓, helium on Spheron C at 4.2°.

The relatively large compressibility of liquid and solid helium suggests that the force field at the carbon black surface compresses or distorts the filled electron shell of the atom, resulting in a diminished cross sectional area for the adsorbed helium atoms. The electron shells of the other inert gases might be expected to behave similarly; however, Emmett, *et al.*,[19] have found it necessary to revise the area of the krypton atom upward when adsorbed as a solid at 78°K. on various surfaces. The differences in behavior of these inert gases can probably be ascribed to the influence of residual motion or zero point energy magnified in the case of helium by its low atomic weight.[20]

A calculation of the heat of adsorption for he-

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[15] W. H. Keesom and Schweers, *Physica*, **8**, 1020 (1941).

[16] W. H. Keesom and K. W. Taconis, *ibid.*, **5**, 161 (1938).

[17] R. M. Barrer, *Proc. Roy. Soc.* (*London*), **A161**, 476 (1937).

[18] R. P. Rossman and W. R. Smith, *Ind. Eng. Chem.*, **35**, 972 (1943).

[19] R. T. Davis, Jr., T. W. DeWitt and P. H. Emmett, *J. Phys. Colloid Chem.*, **51**, 1233 (1947).

[20] W. H. Keesom, "Helium," Elsevier, Amsterdam, Holland, 331 (1942).

lium on carbon black at 4.2°K. has been carried out according to the method described by Giauque and Stout.[2] They calculated the heats of adsorption of helium on $NiSO_4 \cdot 7H_2O$ at 4.2°K. from the Sackur–Tetrode equation assuming a negligible entropy for the adsorbed phase and the ideality of helium at the pressures employed. Thus, the entropy of adsorption becomes equal to the entropy of the gas at 4.2°K.

$$\Delta S_{\mathrm{ads}} = S_{\mathrm{gas}} = R \ln \frac{M^{3/2}T^{5/2}}{P} - 2.317 \qquad (2)$$

The expression for ΔH is then

$$\Delta H = T\Delta S \qquad (3)$$

since ΔF is zero for the isothermal process, gaseous helium at equilibrium pressure, P, to adsorbed helium at pressure, P. Since the pressures (1–650 mm.) employed in the present investigation are considerably higher than those used by Stout and Giauque (10^{-2}–10^{-3} mm.), the assumption of ideality is somewhat suspect. However, heats have been calculated in the manner described above, and are compared in Fig. 4 with those computed from entropies obtained by interpolation of Keesom's data.[21] The latter ΔH values are significantly lower than those calculated on the assumption of ideality only for surface coverages in the second and successive multilayers. Near V/V_m equal to 2.5 the heats approach a limiting value of 33.7 cal./mole, some 12.7 calories greater than the heat of vaporization of 21 cal. mole. If the limiting value of 33.7 cal./mole is used as the heat of vaporization, in conjunction with the B.E.T. c value reported in Table I, a heat of adsorption (E_1) of 56 ± 2 cal./mole is obtained, surprisingly close to the heat of adsorption at the completion of the monolayer as calculated from the aforementioned entropy considerations.

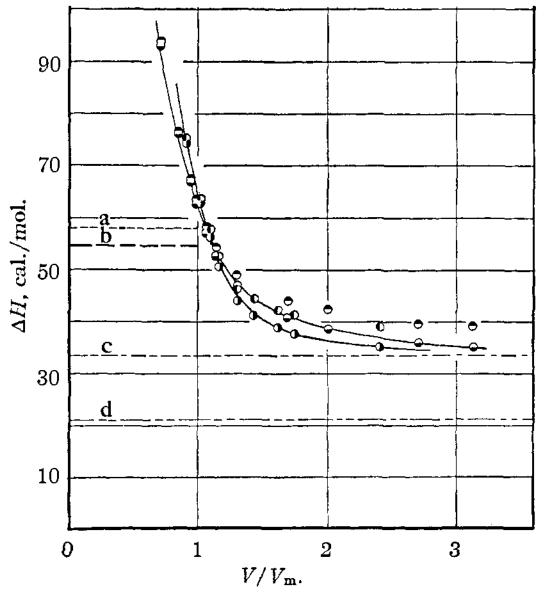

Fig. 4.—Heats of adsorption of helium on Spheron 6 and Spheron C: ◐, Spheron C, ΔH calculated from Sackur–Tetrode equation; ◑, Spheron C, ΔH calculated from Keesom[21]; ◓, Spheron 6, ΔH calculated from Sackur–Tetrode equation; ◒, Spheron 6, ΔH calculated from Keesom[21]; a, — — — —, B. E. T. "heat of adsorption" (E_1), for Spheron C; b, — — —, B. E. T. "heat of adsorption," (E_1), for Spheron 6; c, — - —, limiting value of heat of adsorption; d, — - - —, helium heat of vaporization.

The oxygen chemisorbed on the surface of Spheron 6 carbon black in the form of various complexes[22] is generally considered sufficient (23 cc. S.T.P.) to constitute a monolayer; thus, a comparison of these results with those of Keesom and Schweers[11] employing a glass surface covered with frozen oxygen proves instructive. The calculated differential heats of adsorption of helium at the completion of the first, second, and third layers (V/V_m) on Spheron 6 are 62, 39 and 35 cal./mole, respectively. Keesom and Schweers report heats, determined from the Clausius–Clapeyron equation, on oxygen covered glass to be 62 and 42 cal./mole at the completion of the second and third layers. The agreement is good. In fact, since they assumed a helium diameter of 4.04 Å. in computing surface coverage while 2.80 Å. was employed in the present work, one is perhaps justified in comparing Keesom and Schweers' second and third layer values of 62 and 42 cal./mole with our first and second layer values of 62 and 39 cal./mole. While agreement of this order is doubtless fortuitous, it does lend support to our assumption of negligible entropy for the adsorbed helium.

The fact that both Keesom's and our values for the heat of adsorption of helium remain considerably in excess of the heat of vaporization after a two or three layer coverage, while puzzling, is at least reproducible.

Acknowledgments.—It is a pleasure to acknowledge the coöperation of Arthur D. Little, Inc., and especially the helpful discussions with Dr. H. O. McMahon and Dr. G. King of that organization.

Summary

1. A system of Dewar flasks successfully used for transporting liquid helium with negligible losses is described.

2. The helium isotherms at 4.2°K. on the carbon blacks, Spheron 6 and Spheron C, have been determined, and the application of the B.E.T. equation has been extended to liquid helium temperature.

3. The area of the helium atom adsorbed on carbon black at 4.2°K. is 7.0 ± 0.3 square ångström units.

4. The calculated heats of adsorption of he-

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[21] W. H. Keesom, *ibid.*, p. 247.

[22] W. R. Smith and W. D. Schaeffer, "Proceedings Rubber Technology Conference," London, England, 1948.

lium on Spheron 6 and Spheron C range from 93 to 34 cal./mole.

5. The heat of adsorption, as defined by the B.E.T. "*c*" value is in substantial agreement with the calculated heat curves.

RECEIVED MAY 4, 1948

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Polarographic Study of Cobalt Cyanide Complexes[1]

BY DAVID N. HUME[2] AND I. M. KOLTHOFF

The characteristic properties of a solution of a cobaltous salt in excess alkali cyanide have frequently been attributed to the presence of hexacyanocobalt(II)ate ions.[3] There is much evidence, however, that in at least moderately concentrated solutions the complex which is formed is a pentacyanide rather than a hexacyanide.[4] The oxidation state of the cobalt in these solutions has never been definitely established. In the present investigation, a study of the reduction at the dropping mercury electrode of various cobalt complexes in cyanide medium has led to an understanding of the nature and identity of the complex cobalt ions formed in cyanide medium.

Experimental

The usual polarographic technique was employed. Details of the apparatus and methods have been described in a previous communication.[5] The capillary had a drop time of 3.18 sec. and a value of 1.98 for $m^{2/3}t^{1/6}$ in 0.1*M* potassium chloride at a potential of 0.0 v. against the saturated calomel electrode.

The reduction of cobalt(II) salts in potassium cyanide as a supporting electrolyte was first studied. In agreement with previous investigators[3d,3e] well-defined reduction waves were found for 0.002 *M* cobalt solutions in 0.1 *M* and 1.0 *M* potassium cyanide. The height of these waves was observed to be almost exactly one half that of the corresponding wave in potassium chloride, implying a one-electron reduction (Fig. 1). The shape of the waves obviously indicated irreversibility and no effort was made at analysis. It was also noted that the half wave potential was shifted to more positive values with increasing cyanide concentration, a confirmation of the irreversibility of the electrode reaction. The solutions obtained were yellow-green in color.

Previous investigators had interpreted the apparent one-electron reaction as a reduction of cobalt(III) hexacyanide ion produced spontaneously by water-oxidation of the cobalt(II) hexacyanide ion initially formed. In order to test this hypothesis, pure potassium hexacyanocobalt(III)ate (cobalticyanide) was prepared by the method of Benedetti-Pichler.[6] The product was obtained in large, clear, very pale yellow crystals which dissolved readily in water giving a clear solution. Polarograms were taken on millimolar solutions of the pure complex salt in 0.1 *M* and 1.0 *M* potassium cyanide as a supporting electrolyte.

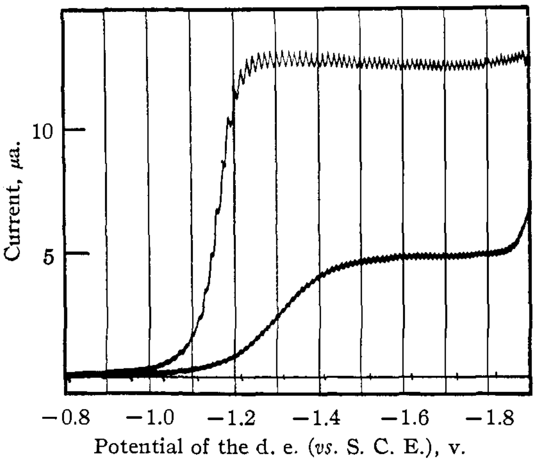

Fig. 1.—Polarograms of 0.002 *M* $CoCl_2$: upper curve in 0.1 *M* KCl; lower curve 1.0 *M* KCN.

No reduction of the cobalt complex could be observed prior to the discharge of potassium ion; the polarograms were identical with the residual current of the cyanide supporting electrolyte. The following experiments were therefore devised to determine the nature of the complex formed by solution of cobaltous salts in alkali cyanide.

A solution of 0.200 millimole of cobaltous chloride in 50 ml. of 1.0 *M* potassium cyanide was titrated amperometrically with 0.100 *M* potassium ferricyanide with exclusion of oxygen. After each addition of reagent and a wait of 2 or 3 minutes, the current at cathode potentials of −0.8 v. and −1.7 v. was measured. The cobalt is not reduced at −0.8 v. but gives a diffusion current at −1.7 v. Ferricyanide is reduced in cyanide medium at all attainable potentials of the dropping electrode, while ferrocyanide gives no wave. Hence any current at −0.8 v. must be due to unreacted ferricyanide. The result is shown in Fig. 2. The ferricyanide was consumed until one mole had been added per mole of cobalt. During the titration, the color of the solution changed from pale yellow-green to deep yellow and the diffusion current at −1.7 v. increased steadily, being approximately doubled by the end of the titration. The wave of the cobalt compound became more drawn-out and the half-wave potential shifted to more negative values (approximately −1.4 v.). The experiment clearly showed, therefore, that cobalt (II) chloride dissolved in excess potassium cyanide solution in the absence of air remains in the divalent state. Furthermore, the oxidized product obtained by treatment with ferricyanide is definitely not cobalt(III) hexacyanide ion, as the latter gives no wave.

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[1] Taken from a portion of the Doctorate thesis of David N. Hume, 1943. Presented in part at the Chicago Meeting of the American Chemical Society, September, 1946.

[2] Du Pont Fellow in Chemistry 1942–1943. Present address: Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

[3] (a) G. Grube and P. Schächterle, *Z. Elektrochem.*, **32**, 565 (1926); (b) R. Peters, *Z. physik. Chem.*, **26**, 217 (1898); (c) T. M. Lowry, *Chem. Ind.*, **42**, 318 (1923); (d) N. V. Emelianova, *Rec. trav. chim.*, **44**, 529 (1925); (e) G. Sartori, *Gazz. chim. ital.*, **66**, 688 (1936).

[4] (a) E. Rupp and F. Pfenning, *Chem. Z.*, **34**, 322 (1910); (b) P. Edelmann, "Dissertation," Dresden T. H., 1915, p. 44; (c) E. Müller and H. Lauterbach, *Z. anal. Chem.*, **62**, 23 (1923); (d) E. Müller and W. Schlüttig, *Z. anorg. allgem. Chem.*, **134**, 327 (1924); (3) S. Glasstone and J. C. Speakman, *Analyst*, **55**, 93 (1930).

[5] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **65**, 1897 (1943).

[6] A. A. Benedetti-Pichler, *Z. anal. Chem.*, **50**, 257 (1927).