[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE MEASUREMENT OF OXIDATION POTENTIALS AT MERCURY ELECTRODES.

II. THE CHROMIC-CHROMOUS POTENTIAL.

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Among important oxidation potentials hitherto undetermined with special precautions is that of a mixture of chromic and chromous ions in aqueous solution. Peters[1], evidently working with platinum electrodes, which, as will be shown below, are unsuitable for this combination, was unable to secure constant and reproducible results. Mazzuchelli,[2] using electrodes of tin, copper and mercury, fared much better, but his values, as will be pointed out, failed to show clearly the relation between concentrations and electromotive force, as will be clear from the points marked M in Fig. 4. In view of the evident adequacy of mercury electrodes as used by one of us[3] in determining the stannic-stannous potential, it appeared worth while to extend the method to a study of the chromic-chromous potential also.[4] Although the general plan of attack was similar to that described in the previous paper, important modifications were necessitated at all stages of the process by the unstable nature of the solutions.

Mercury was purified by passing it in a very finely divided condition many times through a six-foot tower of mercurous nitrate solution.[5] A treatment followed in general by distillation *in vacuo*. All samples were compared before use with one prepared in small quantity by heating red oxide of mercury[6] and redistilling the product. This was dissolved in redistilled nitric acid and thrown down upon a small platinum cathode, thoroughly washed, and then made an anode for a long time with a very weak current. This product proved more noble, by a few tenths of a millivolt, than the metal used for the electrodes in all our cells, including several samples kindly loaned by other investigators. Lewis[6] has shown the vital necessity of the highest degree of purity in mercury if evolution of hydrogen is to be avoided at potentials comparable with those measured by us. . Peters and Mazzuchelli both noted such an evolution on mercury in contrast to our own experience when using pure mercury. McBain[7] also states that pure mercury does not decompose solutions of chromous chloride.

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[1] *Z. physik. Chem.*, 26, 193 (1898).

[2] *Gazz. chim. ital.*, 31, II, 374 (1901); 35, I, 417 (1905).

[3] THIS JOURNAL, 36, 2030 (1914).

[4] See also Bancroft, *Trans. Am. Electrochem. Soc.*, 29, 121 (1916).

[5] See, for instance, Hildebrand, THIS JOURNAL, 31, 933 (1909).

[6] Lewis, *Proc. Am. Acad.*, 41, 399 (1906).

[7] *Inaugural Dissertation*, Heidelberg, 1909.

Chromous chloride was prepared by the method of Moberg[1] and of Peligot[2] by heating sublimed violet chromic chloride at about 400° in a stream of hydrogen. A tube of transparent quartz was ground at both ends into joints of soft glass, and heated with a nichrome spiral. The hydrogen was prepared by electrolyzing sodium hydroxide, free from carbonate, between platinum anodes and copper cathodes. It was dried by sulfuric acid containing chromic acid to avoid reduction, passed over heated copper to eliminate free oxygen, and dried again by phosphorus pentoxide. Chromic chloride labelled "Merck, puriss." was resublimed in a stream of dry chlorine in the above-mentioned quartz tube. It was proved free from iron by oxidation in ammoniacal solution with perhydrol, filtration, and extraction of the filter paper with dilute acid. The filtrate was tested with sulfocyanate. Samples not thus resublimed and containing 0.005% Fe, as estimated colorimetrically, gave the same potentials within the limit of error of measurement. It was also proved that the resublimed samples could be intentionally contaminated with considerable ferrous iron without changing these potentials. Therefore the troublesome process of sublimation was usually omitted.

Tenth-normal hydrochloride acid was prepared from the constant boiling solution[3] distilled, made up volumetrically, and analyzed gravimetrically as a check.

Carbon dioxide for the protection of the solutions during the various manipulations was prepared in a large Ostwald generator. Oxygen was removed by passing the gas through five Emmerling towers containing glass beads moistened with a solution of cuprous chloride in concentrated hydrochloric acid. After being freed from acid by potassium bicarbonate solution, it was carefully dried, and passed over copper gauze in hard glass tubes electrically heated to redness. When used to protect solutions in the cells from oxidation, it was finally bubbled through a solution containing hydrochloric acid of the same concentration as that used in these cells.

The chromous chloride, containing variable amounts of chromic chloride intentionally left unreduced, was dissolved and filtered into the cells, with rigid exclusion of air. The necessary apparatus is shown in Fig. 1. The solid was raked out through the end of the quartz reduction tube A with a bent glass rod introduced through B. A rapid current of hydrogen precluded the entrance of air. The solid fell through the tube C into the bottle D, containing 0.1 *N* hydrochloric acid to repress hydrolysis. This liquid was cooled by a freezing mixture and rapidly stirred during the process by the glass paddle E. This precaution was necessary to avoid the formation of a green complex chromous chloride observed by Prudhomme[4]

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[1] Moberg, *J. prakt. Chem.*, 29, 175 (1843).

[2] Peligot, *Ann. chim. phys.*, [3] 12, 528 (1844).

[3] Hulett and Bonner, THIS JOURNAL, 31, 390 (1909).

[4] *Bull. soc. ind. Mulhouse*, 59, 603 (1889).

and investigated by Knight and Rich.[1] The paddle was provided with a mercury seal F which rendered it gas-tight. A small residue, apparently of chromic oxide, remained undissolved. This was allowed to settle, and then the solution was siphoned off into the funnel G surrounded by a larger glass funnel provided with the ground glass joint H. The filtrate was caught in the bottle I, provided with stirrer and seal, and tube J bearing a sealed-in platinum wire to connect with the mercury M which was to serve as electrode. Other openings in the stopper served for the introduction of carbon dioxide and for the removal of samples for analysis. The funnel tube was next replaced with a siphon tube leading through an intermediate solution of 0.1 *N* hydrochloric acid to the calomel electrode as shown in Fig. 2. Calomel electrodes in 0.1 *N* hydrochloric acid were frequently made up according to the general directions given by Ostwald-Luther[2] and checked against each other to guard against the change in electromotive force with time noted by Sauer,[3] and also by Clarke, Myers and Acree.[4] An excess pressure of carbon dioxide was maintained through the tube K (Fig. 2) as was apparent from the difference in the level of the two mercury surfaces in the seal. The system was finally placed in a thermostat at 25°, and measurements of electromotive force begun.

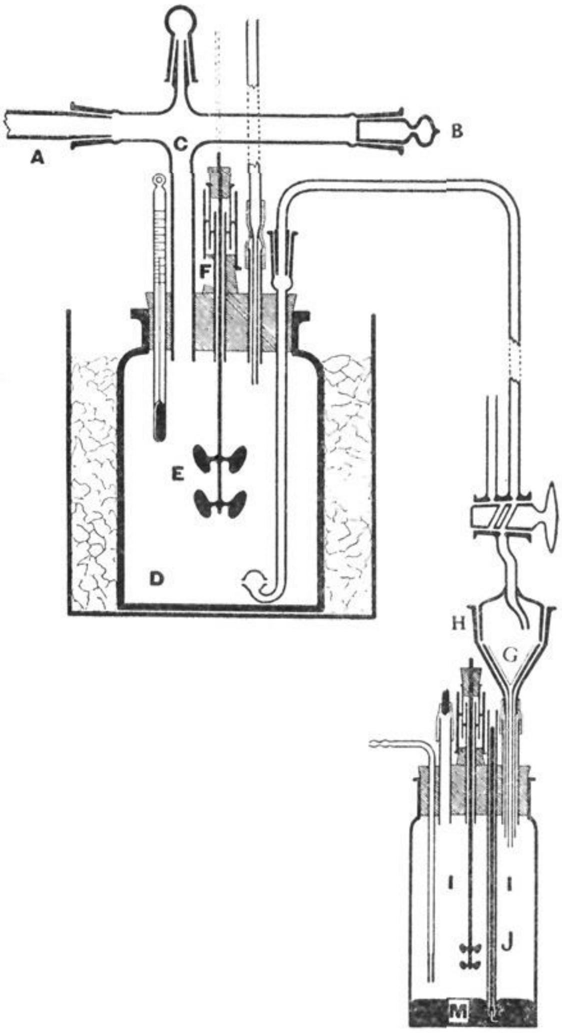

Fig. 1.

For this purpose a Wolff potentiometer of 20,000 ohms resistance was used in connection with a sensitive Leeds and Northrup galvanometer, type H, and a standard cadmium cell frequently compared with a similar cell which had been certified by the Bureau of Standards, and kindly loaned by Mr. E. K. Carver of this laboratory.

In all cases where air was rigorously excluded, the electromotive force increased steadily during a period of approximately thirty-six hours to a

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[1] *J. Chem. Soc.*, **99**, 87 (1911).

[2] *Physiko-chemische Messungen*, p. 442.

[3] *Z. physik. Chem.*, **47**, 146 (1904).

[4] *J. Phys. Chem.*, **20**, 243 (1916).

limiting and constant value which was adjudged to be the reversible potential of the combination. Evidence in support of this view was twofold. First, the introduction of a small amount of mercuric chloride greatly depressed the potential, but this regained very nearly the original maximum on standing for a short time. Secondly, this value was practically the same whether the solution was stirred or not, whereas violent fluctuations occurred on stirring before the maximum was attained. The most plausible explanation of the latter phenomenon is made by assuming residual traces of oxygen present in the original solution. Anderson and Riffe[1] hold that considerable amounts of oxygen can escape reduction by chromous chloride. While we are frankly puzzled by this statement made with reference to concentrations of oxygen capable of volumetric measurement, it might easily hold for the incredibly small pressures of oxygen in equilibrium with our electrodes. An oxygen electrode at —0.40 volt referred to the normal hydrogen electrode as zero, requires a pressure of $10^{(-1.18 + 0.40)/0.015}$ or 10^{-105} atmosphere of oxygen over it. We inferred that the excess over and above the corre-

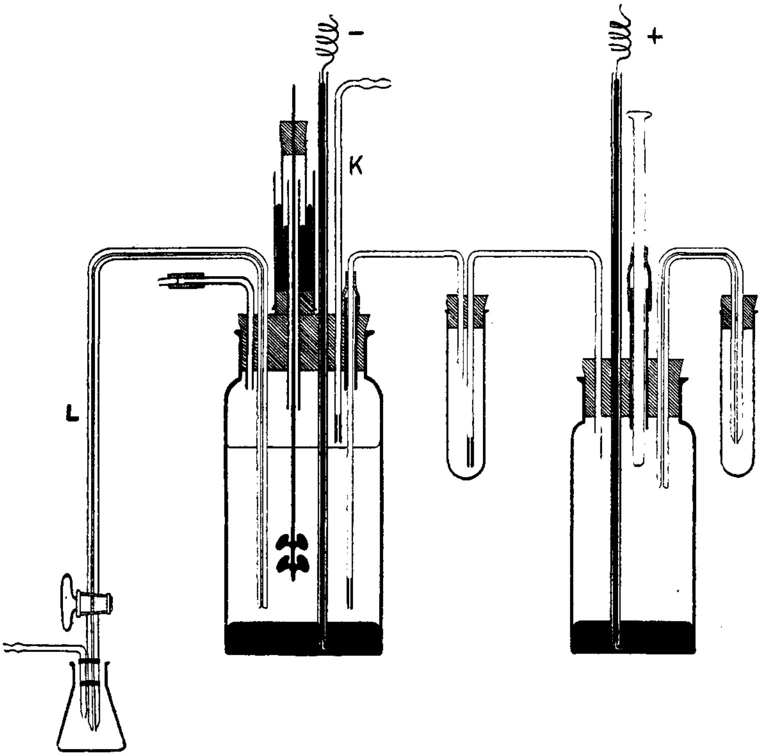

Fig. 2.

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[1] *J. Ind. Eng. Chem.*, 8, 24 (1916).

sponding concentration of oxygen in solution was gradually eliminated by catalytic action on the mercury surface, or at least reduced until it could be polarized on completing a circuit through the cell.

Even the presence of a pinhole in a rubber connection carrying to the cell a stream of carbon dioxide at a pressure considerably greater than atmospheric, permitted inward diffusion of sufficient oxygen to depress the potential of the cell by many centivolts. Two sets of observations, involving leakage of air, are so designated in Fig. 4. We believe that a more sensitive test for the presence of oxygen in a gas otherwise incapable of reacting with the substances in the cell could scarcely be devised. The problem of excluding oxygen with the requisite degree of thoroughness was solved only after months of disappointing labor.

Lamb[1] has shown that the change from the green chromic chloride, which is formed when the anhydrous salt is first dissolved in water, to the violet modification, which is more stable at 25°, is greatly retarded by the presence of free acid. Although the solutions in our cells were violet by the time that the potentials became constant, it is doubtful whether the concentration of the violet modification had then reached its maximum. The fact that constancy was attained, however, seems to show that completion of the reaction would not have affected the potential further.

Fig. 3 shows the course of the potential in a special experiment on mercury and also on platinum. It will be noted that a limiting value is much

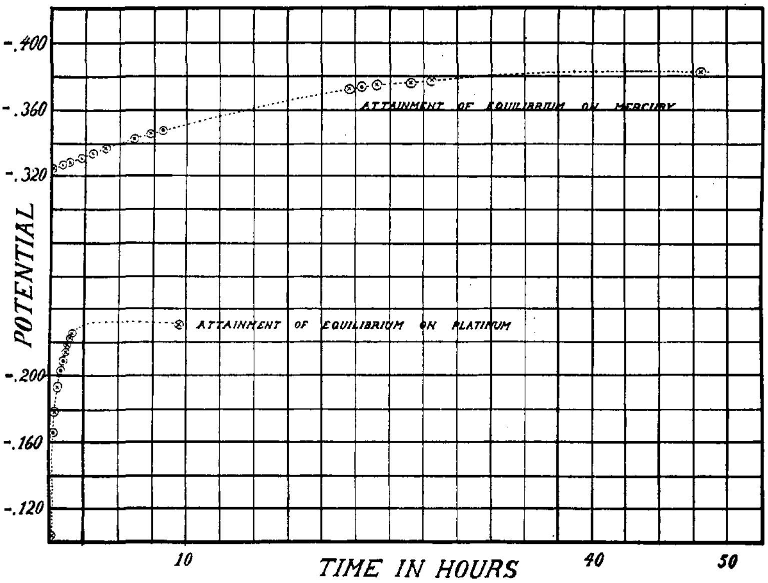

Fig. 3.

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[1] THIS JOURNAL, 28, 1712 (1906).

more rapidly attained on the latter metal, but this occurs with evolution of hydrogen, as was also noted by McBain.

$$2Cr^{\cdot\cdot} + 2H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + H_2.$$

No true equilibrium can be reached under such circumstances. Jablczynski[1] has suggested a plausible explanation of this phenomenon. The more rapid increase in potential on the platinum electrodes as compared with mercury electrodes suggests that the catalytic reduction of oxygen on platinum occurs more readily than on mercury. The value noted on platinum corresponds roughly to that recorded by Peters, who used electrodes of the same material.

After attainment of the maximum potential on mercury, samples were withdrawn through the siphon tube L (Fig. 2) into weighed Erlenmeyer flasks of 50 cc. capacity filled with carbon dioxide. A correction was made for the weight of carbon dioxide displaced by the solution. In the determinations of chromous concentration the flasks contained known weights of standard potassium dichromate solution carefully freed from air. A steady stream of pure carbon dioxide was maintained throughout the operation. The residual dichromate was titrated with standard ferrous ammonium sulfate from a weight buret, the end point being determined electrometrically because of the intense color of the solutions.[2] The chromous salt was equivalent to the amount of dichromate reduced. It was shown by special experiments that if the oxygen was not removed from the dichromate solution, it oxidized almost the calculated quantity of chromous salt.

A and B Solution of $CrCl_2$ run into oxygen-free $K_2Cr_2O_7$ solution + 20 cc. of oxygen-saturated water.

C and D Solution of $CrCl_2$ run into oxygen-free $K_2Cr_2O_7$ solution + 20 cc. of air-saturated water.

Experiment.	A (g.).	B (g.).	C (g.).	D (g.).
$CrCl_2$ solution	13.033	9.714	9.124	10.357
Dissolved O_2 present	0.00091	0.00091	0.00018	0.00018
Cr^{II} oxidizable by dissolved oxygen	0.0059	0.0059	0.0012	0.0012
Cr^{II} found, total	0.0948	0.0709	0.0699	0.0788
Cr^{II} corrected, total	0.1007	0.0768	0.0711	0.0800
Cr^{II} found, per g. solution	0.00727	0.00730	0.00766	0.00761
Cr^{II} corrected, per g. solution	0.00772	0.00791	0.00779	0.00772
Mean, uncorrected	0.00728		0.00763	
Mean, corrected	0.00781		0.00775	

If correction for dissolved oxygen is made, the results become nearly uniform in both cases. If no correction is made, the chromous concentration appears far too small. This evidence tends to show that the reaction between chromous chloride and oxygen is exceedingly rapid and complete.

Total chromium was determined in other portions of the solution.

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[1] *Chem. Zentr.*, 79, II, 576 (1908).

[2] Forbes and Bartlett, THIS JOURNAL, 35, 1535 (1913).

These were treated, in inclined Kjeldahl flasks, with excess of sodium peroxide and boiled for 45 minutes. Blank experiments showed this time sufficient to decompose all the excess of peroxide. Then the solutions were acidified, transferred to a beaker, and titrated electrometrically with ferrous ammonium sulfate. Chromic salt was determined by difference between total chromium and chromous salt.

The standard ferrous ammonium sulfate solution was 0.05 *N*. It was kept in an atmosphere of carbon dioxide, and frequently restandardized. The density of the solution from each cell was determined, and all analytical results expressed in milli-equivalents per liter. A gram equivalent of chromium, either in the chromic or the chromous condition, equals the gram atom.

The observed potentials of the cells were first corrected by subtracting 0.003 volt, which was found to be the diminution in potential resulting from the introduction of saturated potassium chloride at the liquid junction. This correction is so small that the conditions under which the boundary between the liquids was formed are unimportant. The chromic-chromous potentials, referred to the normal hydrogen electrode as zero, were then calculated by subtracting 0.336[1] volt from the corrected cell potentials.

COMPOSITION AND POTENTIALS OF CHROMIC-CHROMOUS SOLUTIONS ON MERCURY.

Cell No.	G. per liter. Cr.	Cr^{II}.	Cr^{III}.	Log Cr^{III}/Cr^{II}.	Time in hours.	π as observed.	Single potential. π.
1	2.364	2.123	0.241	−0.945	68	0.801	0.462
2	2.308	1.949	0.359	−0.735	19	0.786	0.447
3	4.610	3.153	1.457	−0.335	45	0.757	0.418
4	1.824	1.176	0.648	−0.259	45	0.751	0.412
5	1.974	0.774	1.200	+0.191	53	0.727	0.388
6	1.973	0.773	1.200	+0.189	73	0.726	0.387
7	4.400	0.773	3.627	+0.672	12	0.693	0.354
8	1.668	1.085	0.583	−0.271	..	0.753	0.414

Cell 8 was set up and measured by Mr. G. H. Priest of this laboratory.

The chromic chloride used in cell No. 4 was resublimed in chlorine. Cells No. 3 and No. 7 show effect of doubling concentration of chromium. Cell No. 7 also shows that the addition of chromic chloride to a solution of chromous and chromic chlorides in equilibrium produces results in accord with the theory, since this result was obtained by adding chromic chloride to cell No. 6.

The single potentials are plotted against the logarithm of the concentration ratio in Fig. 4. Mazzuchelli's results, obtained in normal acid solution, and referred by us to the same standard of potential, are plotted separately by the points marked M.

Experiments were instituted by us, and continued by Mr. G. H. Priest

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[1] Loomis, *J. Phys. Chem.*, 19, 660 (1915).

to determine the values of the potential in normal acid solution, keeping the total Cr concentration as heretofore. Great difficulties were encountered by reason of the increased tendency of the solution to decompose, and only two out of a large number of cells fulfilled in any sense the requirements for equilibrium as stated above. The corresponding potentials are indicated in Fig. 4. If a straight line connecting these points be produced, it would intersect the curve of potentials in tenth-normal acid when $Cr^{III}/Cr^{II} = 1/3$, suggesting that under these conditions the relative degrees of dissociation are constant in spite of a ten-fold change in acid concentration. The improbability of this conclusion, as well as the unsatisfactory behavior of the cells, leads us to mistrust the results in normal acid. If reliable figures in normal acid were at hand, it would be possible to extrapolate our potentials to zero acid concentration.

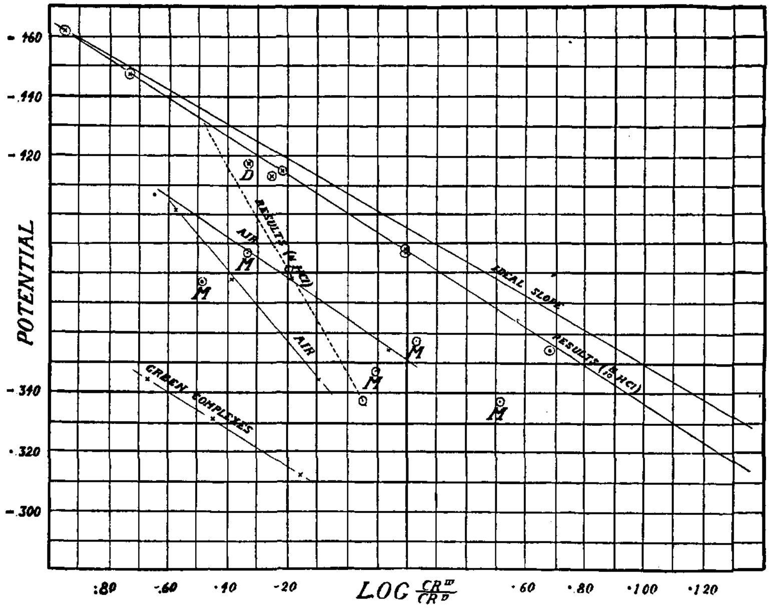

Fig. 4.

The point indicated by the letter D represents the potential found on doubling the usual concentration of total chromium 0.1 N acid. Apparently the smaller variations, such as existed in the other measurements, would be negligible.

The observed slope of the line is 0.065 as against the theoretical value 0.058. Data on complex formation and repression of ionization of chromic and chromous chlorides in the presence of hydrochloric acid and of each other are not present at available. Therefore, no values for chromic and chromous ion concentrations are given, and an explanation of the somewhat unimportant deviation of the slope of the line from the ideal value must also be postponed.

It has been mentioned above that a green chromous complex resulted if the solution of anhydrous chromous chloride did not take place at the lowest possible temperature. Early experiments in which the solution was prepared by pouring 0.1 *N* acid at room temperature upon the anhydrous salt led to green solutions giving true equilibrium potentials about a tenth of a volt lower than those obtained by raking anhydrous salt into chilled acid, with stirring.

Cr^{III}/Cr^{II} by analysis.	Single potential π.	Cr^{III}/Cr^{II} from π.
0.21	0.344	7.4
0.35	0.331	12.1
0.69	0.312	24.0

These points are shown on a separate curve. In other words only about three per cent. of the total chromous salt appears to be dissociated from the complex as chromous ion.

Summary.

Pure violet $CrCl_3$, partially reduced to $CrCl_2$ by purified hydrogen at 400° in quartz, was dissolved with stirring in ice-cold, 0.1 *N* hydrochloric acid. The solution, filtered into the cell, was allowed to stand over pure mercury. If all operations were conducted in hydrogen or carbon dioxide absolutely free from oxygen, the potential rose throughout two days to a constant maximum, otherwise it fluctuated irregularly. Concentrations at equilibrium were determined analytically. Referred to normal hydrogen electrode as zero, with correction for junction potentials,

$$\pi = -0.400 + 0.065 \log Cr^{III}/Cr^{II}.$$

On platinum, potentials reached a maximum about 0.16 volt lower, with evolution of hydrogen.

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THE DRAINAGE OF CRYSTALS.

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In the course of an attempt[1] to separate isotopic forms of lead nitrate by fractional crystallization, a question arose as to the desirability of centrifugal drainage as a means to the speedier separation of substances of nearly identical solubilities. As no exact treatment of the matter was known to us, the following discussion was developed, and is presented here in the hope that it may interest chemists who are undertaking the separation or purification of substances by crystallization:

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[1] Richards and Hall, THIS JOURNAL, 39, 531 (1917).