termine which planchets were to be combined to form the various rare earth fractions. No sample of eluate escaped combination. The identity of the activities obtained, together with the radiochemical purity, was determined by standard decay and absorption measurements.

Results and Discussion

Mayer and Freiling[1] have shown that the use of 1 *M* lactic acid at *p*H 3 was sufficient to give complete separation of Eu and Sm in a reasonable time. The separation of Gd from Eu, and particularly the detection of minute amounts of Tb^{161} activity in the presence of large amounts of Y^{91} activity, require even better separations. To achieve these separations and still hold the time required for a run down to a reasonable value, use was made of discontinuous gradation in eluant strength. The best result of a number of trials is illustrated by the elution history curve in Fig. 1. These separations were obtained by eluting with 10 ml. of 0.85 *M* lactic acid, 10 ml. of 0.90 *M*, 10 ml. of 0.95 *M*, and using 1 *M* lactic acid for the remainder of the run. The extent of decontamination of each rare earth from its nearest neighbors is presented in Table I.

TABLE I

DECONTAMINATION OF RARE EARTHS FROM THEIR NEAREST NEIGHBORS IN THE ELUTION PROCESS

Planchets combined	Rare earth activity	Percentage of preceding activity in sample	Percentage of following activity in sample
11-18	Y^{91}	. .	n.d.[a]
19-27	Tb^{161}	0.15	n.d.
28-34	Gd^{159}	n.d.	n.d.
35-41	Eu^{156}	n.d.	n.d.
42-56	Sm^{153}	0.3	n.d.
57-68	Pm^{149}	n.d.	0.01
69-98	Nd^{147}	n.d.	n.d.
. .[b]	Pr^{143}	n.d.	. .

[a] n.d. stands for none detected. [b] Eluate containing Pr was received in a beaker.

It is evident from the shape of the Nd peak, and especially the Sm peak, that the column was overloaded under these conditions. The use of wider columns and proportionately higher flow rates would be expected, therefore, to give still better separations in the Pm–Nd region without increasing the expenditure of time.

Treatment of duplicate samples has yielded the results shown in Table II. These data are comparable in precision to any radiochemical analytical results and illustrate the possibility of using this method to obtain much more accurate values of rare earth fission yields than those appearing in the current literature.[2]

TABLE II

COMPARISON OF RESULTS FROM DUPLICATE SAMPLES

Rare earth activity	Counts per minute per total sample × 10^{-5}	
	1	2
Eu^{156}	0.323	0.330
Sm^{153}	2.28	2.30
Pm^{149}	10.00	10.03
Nd^{147}	14.2	14.4

The source of the Tb and Gd activity found in these runs is unknown. Neither Tb nor Gd activity has been discovered among the fission products. The relative amounts of activity are such that they could reasonably have been formed either by fission or by neutron activation of microgram amounts of Gd impurity. We are presently engaged in the process of attempting to determine their source.

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NUCLEAR AND PHYSICAL CHEMISTRY BRANCH
U. S. NAVAL RADIOLOGICAL DEFENSE LAB.
SAN FRANCISCO 24, CALIFORNIA

The Densities and Thermal Expansion Coefficients for Cobaltous Chloride Hexahydrate and Ethyl Iodide[1]

BY DWIGHT A. HUTCHISON

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Some years back Sampson and Bleakney[2] reported the existence of a stable cobalt isotope, Co^{57}, to the extent of one part in 600 of Co^{59}. The later work of Mitchell, Brown and Fowler[3] showed that if Co^{57} exists, it could occur to an extent no greater than one part in 30,000 of Co^{59}. In the years 1940–1946, the writer was concerned with the experimental determination of precise absolute[4] and relative[5] densities of certain crystals, the relative densities being used to determine the efficiencies of electrolytic separations of isotopes. The dual purpose, to detect the existence of Co^{57} and, if found, to determine the extent of its electrolytic separation from Co^{59}, formed the basis for the present experimental work. Although the original purposes were found untenable because sufficient precision in the relative density of $CoCl_2 \cdot 6H_2O$ could not be attained without a tremendous expenditure of time, a large amount of the present work was already completed before such conclusions could be made.

Inasmuch as the experimental results obtained may be of help to some workers in connection with other problems, it was felt worthwhile to present the experimentally determined densities and expansion coefficients for $CoCl_2 \cdot 6H_2O$ and C_2H_5I.

The experimental technique of the determination of the densities of certain solid compounds has been described previously.[4] The method consists of suspending crystals of the substance, the density of which is to be determined, in a liquid of proper density. After a density–temperature determination of the suspension liquid, the temperature at which the solid crystal is suspended in the liquid forms the basis for obtaining the density of the solid.

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(1) This paper is a technical report of work done in the Chemistry Department and the State Engineering Experiment Station of the Georgia Institute of Technology, Atlanta, Georgia.

(2) M. B. Sampson and W. Bleakney, *Phys. Rev.*, **50**, 732 (1936).

(3) J. J. Mitchell, H. S. Brown and R. D. Fowler, *ibid.*, **60**, 359 (1941).

(4) H. L. Johnston and D. A. Hutchison, *ibid.*, **62**, 32 (1942). D. A. Hutchison, **66**, 144 (1944).

(5) D. A. Hutchison, *J. Chem. Phys.*, **14**, 401 (1946); D. A. Hutchison, *ibid.*, **13**, 536 (1945); H. L. Johnston and D. A. Hutchison, *ibid.*, **10**, 469 (1942).

The literature values for the density of $CoCl_2 \cdot 6H_2O$ range from 1.84 to 1.924. The latter value[6] which, apparently, is the most accurate to date, is larger than the present result by 0.7%.

Precise data for the density and cubical thermal expansion coefficient of one of the suspension media, C_2H_5I, was also obtained. The values recorded in the literature for C_2H_5I are particularly discordant. Previous data[7] yield $\rho_{25°} = 1.924 \pm 0.002$ g.-cm.$^{-3}$, which is larger than that obtained here by 0.7%, and $\alpha = 1.171 \pm 0.003 \times 10^{-3}$°C.$^{-1}$ from 0–63°, which is larger by 0.2%.

Experimental Description

Purification of Cobaltous Chloride.—The starting material employed was Merck and Co., Inc., reagent grade $CoCl_2 \cdot 6H_2O$ which contained about 0.30% alkali and alkaline earths and about 0.50% of nickel plus small amounts of other impurities. Approximately one pound of starting material was dissolved in water to saturation at room temperature and fractionally crystallized by standing overnight. About the first half of the material crystallized was used to prepare the solution for the next crystallization. Four crystallizations were required to effect agreement in density within the precision attained between different batches of starting material. As a precautionary measure, six crystallizations were made for all crystals. Crystallizations were performed in a dry-box through which air was passed which was filtered with clean glass wool and dried by passage over calcium chloride.

Pure water employed in the first four crystallizations of $CoCl_2 \cdot 6H_2O$ was obtained by double distillation in a fused silica still from an alkaline permanganate solution and from an acid dichromate solution. For the last two crystallizations water from a further distillation was employed. The latter triply distilled water had a specific conductivity of less than 10^{-7} ohm^{-1}.

The conditions governing the choice, the methods of preparation and the density calibration of the suspension media used in the present work are similar to that used previously and have been described elsewhere.[4]

The Suspension Liquids.—The final compositions of liquids on which precise density calibrations were made were: (a) The 19 to 20° liquid: 90 ml. of ethylene dibromide, 14.8 ml. of *n*-pentyl alcohol and 14.8 of *n*-hexyl alcohol. (b) The 25 to 26° liquid: ethyl iodide. (c) The 27 to 28° liquid: 90 ml. of ethylene dibromide, 12.1 ml. of *n*-pentyl alcohol and 12.1 ml. of *n*-hexyl alcohol.

The ethyl iodide and ethylene dibromide used in the preparation of suspension media were prepared from Merck and Co., Inc., reagent quality C_2H_5I and $C_2H_4Br_2$. The *n*-pentyl alcohol and *n*-hexyl alcohol were prepared from Eastman Kodak Co. practical grade alcohols. The isothermal densities of the suspension media were found to remain constant within the experimental limits of precision ($\pm 5 \times 10^{-6}$ g.-ml.$^{-1}$) of the density determination for a period of at least seven days as evidenced by density recalibrations of the media after a week's time.

Preparation of Suspension Crystals.—Crystals were grown from the purified $CoCl_2 \cdot 6H_2O$ (see above) by dissolving about 25 g. of the material in about 25 ml. of triply distilled water in a Pyrex container. After standing overnight in a dry-box a sufficient number of crystals of varying size had formed such that a number of crystals from 1 to 3 mm. in diameter could be selected which were suitable for suspension in the three suspension liquids.

Unsuccessful attempts to improve the quality of crystals with regard to small cracks, occluded liquid, etc., were made by addition of HCl and C_2H_5OH to the crystallizing solution. Hence, all crystal suspension temperatures reported here were taken on crystals grown from pure water.

Data for Absolute Density.—Twenty-four crystals were suspended in the three different media to determine the suspension temperatures of the purified $CoCl_2 \cdot 6H_2O$. The suspension temperatures are summarized in Table I for the three media. The average suspension temperatures of the crystals in the three media (a), (b) and (c) (see above) are 19.878°, 25.702° and 27.215°, respectively.

By plotting the experimentally determined densities for the three suspension media against temperature, straight lines are obtained. The slopes of these plots for liquids (a), (b) and (c) yield the density–temperature coefficients, -1.908×10^{-3}, -2.233×10^{-3} and -1.916×10^{-3} g.-ml.$^{-1}$-deg.$^{-1}$, respectively. Application of these thermal coefficients, to correct the determined densities of the suspension media to the suspension temperatures of crystals, yielded the average values, 1.91164, 1.90981, 1.90933 g.-ml.$^{-1}$ at 19.878°, 25.702° and 27.215°, respectively.

Utilizing the density–temperature values for the temperature intervals from 19.878° to 27.215° and from 19.878° to 25.702°, we obtain the values for α, the cubical expansion coefficient, 1.649×10^{-4} and 1.645×10^{-4}°C.$^{-1}$, respectively. An arithmetic average of these yields, for the thermal cubical expansion coefficient of cobaltous chloride hexahydrate, the value

$$\alpha_{CoCl_2 \cdot 6H_2O} = 1.647 \pm 5 \times 10^{-4}\text{°C.}^{-1} \text{ (temp. range, 19.9–27.2°)}$$

Employing the above value to correct the three determined densities to 25°, we obtain, for the arithmetic average of these three values, the density

$$\rho_{25.000°} = 1.91009 \pm 0.00034 \text{ g.-cm.}^{-3}$$

In the determination of the above values for the cubical expansion coefficient and density of $CoCl_2 \cdot 6H_2O$, we have employed one pure liquid as one of the suspension media, namely, ethyl iodide. For this liquid the value of the thermal cubical expansion coefficient obtained is $\alpha = 1.1686 \pm 0.0001 \times 10^{-3}$°C.$^{-1}$ (temp. range, 23.0–26.5°) and the density at 25.000° is

$$\rho_{25.0000°} = 1.91133 \pm 0.00003 \text{ g.-cm.}^{-3}$$

Discussion

As in previous determinations[4] the rise and fall of crystals with temperature of the suspension media were observed until the temperature interval between rises and falls could be bracketed to 0.004° and passed over six times with six reversals of the crystal motion. The temperatures in Table I are those at the midpoints of the 0.004° intervals. Differing from previous work, the suspension of $CoCl_2 \cdot 6H_2O$ crystals presented some difficulties, apparently due to an interaction between the suspension medium and the crystal, and probably to a much larger extent to crystal inhomogeneities which were much greater for $CoCl_2 \cdot 6H_2O$ than for NaCl or KCl[4] as shown by the relatively large spread in suspension temperatures given in Table I. The crystal could be bracketed in a 0.004° range, but on the third to fifth reversal the crystal would begin to

TABLE I

SUSPENSION TEMPERATURES OF TWENTY-FOUR CRYSTALS PURIFIED AND GROWN AS DESCRIBED IN TEXT

Liquid a		Liquid b		Liquid c	
Number of crystals suspended	Suspension temp., °C.	Number of crystals suspended	Suspension temp., °C.	Number of crystals suspended	Suspension temp., °C.
1	19.858	1	25.663	1	27.178
1	19.862	1	25.674	2	27.193
2	19.871	1	25.687	1	27.212
5	19.876	1	25.692	3	27.213
6	19.878	2	25.698	3	26.216
4	19.879	4	25.699	5	27.218
3	19.884	5	25.704	5	27.219
1	19.892	4	25.705	3	27.225
1	19.899	3	25.712	1	27.229
		1	25.724		
		1	25.741		
Average	**19.878**	**Average**	**25.702**	**Average**	**27.215**

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[6] G. L. Clark, A. J. Quick and W. D. Harkins, THIS JOURNAL, **42**, 2487 (1920).

[7] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, pp. 27, 28.

drift to a new 0.004° interval. After 3–4 drifts to higher or lower temperatures the crystal would settle to a 0.004° interval over which 6–8 reversals could be obtained. It was this final interval that determined the suspension temperatures listed in Table I.

If the $CoCl_2 \cdot 6H_2O$ crystals were exposed to the atmosphere and examined under a low power microscope, one could observe the formation of the pink anhydrous cobaltous chloride on the surface of the crystal. If a crystal were placed in the suspension media for about 15 minutes, and then withdrawn and examined in a humid atmosphere under the microscope, one observed an initial faint layer of the anhydrous material which would disappear within five minutes.

It would appear that a dehydration of $CoCl_2 \cdot 6H_2O$ was occurring during suspensions which would tend to increase the measured densities. However, the wide spread in suspension temperatures indicates crystal imperfections such as microscopic cracks and occlusions of solution which would tend to decrease measured densities. Differing from previous work[4] it is impossible to exclude crystals with small defects and all suspension temperatures must be included and given equal weight when obtaining the final most probable values of density and errors in density.

The probable errors of the crystal densities obtained from the individual suspension media are approximately one hundredth as large as the probable error computed from the three crystal densities corrected to 25°. Hence, the latter was used in stating the final error to the average of the three densities. Apparently the differences in the three values of the densities at 25°, *i.e.*, (a) 1.91080, (b) 1.90992 and (c) 1.90969, may be explained by the differences in the interactions of the suspension media with the $CoCl_2 \cdot 6H_2O$.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Determination of the Basicity of Very Weak Bases

BY H. H. JAFFÉ

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Pratt and Matsuda have recently described a technique for the determination of the order of basicities of such weak bases as ketones, esters, ethers and alcohols.[1] The basicities were expressed in terms of the rate constants (k) of the self-etherification of benzhydrol in the presence of *p*-toluenesulfonic acid and of the base under a set of rigidly defined conditions. It appears desirable to attempt to derive, from these rate constants, relative values of the equilibrium constants (K_{BH^+}) for the reaction $BH^+ \rightleftharpoons B + H^+$, where B is the base.

Pratt and Draper have examined the self-etherification of benzhydrol in the presence of a small amount of *p*-toluenesulfonic acid, and have found the reaction to be of first order in benzhydrol.[2] These authors also suggested that the reaction is first order in the acid, and that the deviations from this order, which were observed, are due to salt effects.[2] The following arguments are based on the assumption that the reaction is first order in both alcohol and acid. It will further be assumed that all of the strong acid (HA), which is present in low concentration, transfers its protons to the base B or to benzhydrol (C) present in much higher concentration.[3]

We desire to calculate the acid dissociation constant of the conjugate acid of the base (B)

$$K_{BH^+} = [B][H^+]/[BH^+]$$

where the quantities in brackets represent concentrations. $[H^+]$ is given by

$$[H^+] = K_{CH^+}[CH^+]/[C]$$

where K_{CH^+} is the acid dissociation constant of the conjugate acid of C. $[BH^+]$ is given by

$$[BH^+] = [CH^+]^0 - [CH^+]$$

where $[CH^+]^0$ is the concentration of $[CH^+]$ in the absence of the base B. The rate law for the self-etherification is

$$-d[C]/dt = k'[CH^+][C] = k[C]$$

and hence $[CH^+]$ and $[BH^+]$ are proportional to k and $(k^0 - k)$, respectively, where k^0 is the rate in the absence of B, the blank in the notation of Pratt and Matsuda.[1] Then

$$K_{BH^+} = K_{CH^+}\frac{[B]}{[C]}\cdot\frac{k}{k^0 - k} \qquad (1)$$

Since B and C are present in large concentration compared to the other quantities involved in the calculations, [B]/[C] is constant, and equals $^1/_2$ under the conditions of reference 1. Thus, Pratt and Matsuda's method combined with equation 1 permits evaluation of relative values of the acid dissociation constants of the conjugate acids of very weak bases in benzene solution.

Pratt and Matsuda[1] have shown that a correlation exists between Hammett's substituent constants (σ) and the relative basicities of substituted acetophenones and ethyl benzoates, as expressed by the rate constants of the self-etherification reaction. It is of interest to note that the relative values of K_{BH^+} obtained by use of equation 1 are much better represented by the Hammett equation than the rate constants of reference 1. The reaction constants calculated from the K_{BH^+}-values obtained

TABLE I

COMPARISON OF LITERATURE VALUES OF RELATIVE ACID DISSOCIATION CONSTANTS WITH VALUES CALCULATED BY USE OF EQUATION 1

Compound	$K/K_{C_6H_5COCH_3}$ From eq. 1	 From lit.
p-$CH_3C_6H_4COCH_3$	0.79	0.21[a]
p-$BrC_6H_4COCH_3$	1.5	4.3[a]
$C_6H_5COOCH_3$	2.0	18[b]
$C_6H_5NO_2$	24[c]	25,000[d], 180,000[b]

[a] From reference 6. [b] From reference 7. [c] Too much significance should not be attached to this value. The denominator in equation 1 is about 3% of k^0, and both k and k^0 are known only to ±2%. [d] From reference 8.

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(1) E. F. Pratt and K. Matsuda, THIS JOURNAL, **75**, 3739 (1953).

(2) E. F. Pratt and J. D. Draper, *ibid.*, **71**, 2846 (1949).

(3) The same conclusions would be reached on the basis of the alternate assumption that all of the acid HA is involved in formation of complexes with the base B and benzhydrol (C), which appears more reasonable for solutions in the non-polar solvent benzene.