[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Distribution of Minute Amounts of Material between Liquid Phases

BY D. C. GRAHAME AND G. T. SEABORG

It frequently happens in chemical investigations that a knowledge of the behavior of very small amounts of material in solution, either alone or accompanied by larger amounts of other substances, becomes of considerable importance. Particularly in the use of radioactive substances as indicators for chemical investigations or in the identification of newly discovered artificially prepared radioactive isotopes is it desirable to know what chemical behavior may be expected of minute quantities of radioactive matter in the absence of appreciable amounts of its inactive isotopes. The work of Fajans, Paneth, Hahn and others[1] has led to the formulation of rules concerning the adsorption or coprecipitation of minute amounts of material upon precipitates formed under various conditions. Studies of this sort lead to qualitative conclusions only and do not permit any very accurate prediction as to the behavior of untried substances. It seemed likely, on the other hand, that minute amounts of material would distribute themselves between liquid phases in a simple manner owing to the absence of adsorption phenomena so characteristic of the solid phase. It could not be foretold, of course, whether the walls of the containing vessel or the dust particles inevitably present in the solution would exhibit sufficient adsorption of the microcomponent to influence the experimental results.

I. Partition of Gallium Chloride between Ether and Hydrochloric Acid

Experimental Details.—Ether (99.5%) was dried with anhydrous calcium chloride and metallic sodium, then distilled in an all-glass still (b. p. 34.4 ± 0.2°). Hydrochloric acid, 6 *N*, was distilled in an all-glass still and shaken with ether to remove possible traces of gallium chloride. Chemically pure zinc chloride was dissolved in 6 *N* hydrochloric acid and freed from gallium by repeated extractions of gallium chloride with fresh ether prepared as above. The solution so prepared was evaporated to remove hydrochloric acid, redissolved in doubly-distilled water and electrolyzed between a carbon cathode and platinum anode to give a thin deposit of gallium-free zinc. The zinc was bombarded in air with 8.0 Mev deuterons from the Berkeley cyclotron to form, among other things, radioactive isotopes of gallium. From the intensity of the radioactivity produced ($\sim 10^{-2}$ millicuries of sixty-eight minute gallium) we estimate that the amount of gallium formed was about 10^{-12} g.[2] The sample of zinc containing this gallium was dissolved in 6 *N* hydrochloric acid (prepared as above) and shaken with 25 cc. of ether, whereby most of the radio-gallium was extracted as gallium chloride.

This ether extract was shaken several times with 6 *N* hydrochloric acid (saturated with ether) to remove traces of zinc chloride from the ether solution after which the distribution ratio of the gallium chloride remaining in the ether was determined in the following manner. To the ether solution in a cylindrical separatory funnel an approximately equal volume of 6 *N* hydrochloric acid (saturated with ether) was added. The mixture was brought to a temperature of 20.0 ± 0.1° in a water thermostat and shaken thoroughly to establish equilibrium between the liquid phases. After the volumes had been marked, the aqueous layer was drawn off very carefully into a second separatory funnel and shaken again at 20° with an equal volume of ether already in equilibrium with 6 *N* hydrochloric acid. The two ether extracts thus obtained were evaporated to dryness on shallow copper trays of identical size and shape which could be placed in a reproducible manner under a Lauritsen type quartz fiber electroscope or under a thin-walled Geiger–Müller counter. In order to obtain a fairly uniform deposit on the copper trays, a few drops of alcohol were added to the ether during the evaporation process and the solution was rocked back and forth by hand during the final stages of the evaporation. Gentle heating hastened the evaporation, but the solution was not boiled.

The ratio of the intensities of the radiations from the radioactive gallium on the trays gave a measure of the relative amounts of gallium chloride present in the two ether extracts. From this ratio and a knowledge of the volumes of the ether and aqueous phases, it was possible to calculate by a method of successive approximations the distribution ratio of the gallium chloride between the two liquid phases. Because of the extreme thinness of the deposits on the trays self-absorption of the radiation by the body of the sample did not need to be considered in most instances. In certain experiments, however, the amount of material present in the trays was sufficient to absorb an appreciable fraction of the β-particles emitted by the sample. In such cases the relative intensities were estimated with a Geiger counter under conditions such that only γ-rays were detected. The counting rate was then practically independent of the thickness of the samples over the range of thicknesses used.

Results.—There are two known isotopes of gallium formed by the bombardment of zinc with deuterons, with half-lives of sixty-eight minutes

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(1) A summary and discussion of these investigations is found in Hahn's "Applied Radiochemistry," Cornell University Press, Ithaca, N. Y., 1936.

(2) This estimate also takes into account the fact that other isotopes of gallium (radioactive and non-radioactive) are formed during the bombardment.

and eighty-three hours, respectively. Both were observed in these experiments (in addition to another which will be mentioned later), and since a distribution coefficient for gallium chloride could be obtained from either, measurements were made with one or the other or both. The results obtained are presented in Table I. Column 2 gives the approximate molal concentration of gallium chloride in the ether phase of the first extract. Column 3 gives the half-life of the radioactive body on which the experiment was conducted, and column 4 gives the distribution coefficient, K, expressed as the ratio of the molal concentration in the ether phase to that in the aqueous phase in equilibrium at 20°. The probable error in the distribution coefficient, estimated from the internal consistency obtained in duplicate runs, is about $\pm 10\%$. Experiment 4 differed from the others in that 7 mg. of gallium chloride was added to the radioactive sample at the beginning of the experiment. The result so obtained indicates that the distribution of gallium chloride between ether and hydrochloric acid is the same at extremely low concentrations of gallium chloride as at ordinary concentrations.

TABLE I

DISTRIBUTION RATIO OF GALLIUM CHLORIDE BETWEEN ETHER AND HCl (~ 6 N)

Expt.	Initial concn. of $GaCl_3$	Half-life	Distribution ratio K
1	$\sim 10^{-12}$	68 min.	18.1
2	$\sim 10^{-12}$	83 hr.	19.0
3	$\sim 10^{-12}$	68 min.	17.5
4	0.0016	83 hr.	16.9

II. Distribution of Manganous Chloride between Ether and Hydrochloric Acid

Experimental Details.—A solution in ether of manganese-and-cobalt-free ferric chloride was prepared by dissolving sublimed ferric chloride in ether and extracting manganese and cobalt by repeatedly shaking the solution with fresh, triply-distilled (in Pyrex) 6 N hydrochloric acid. The experiments to be described show that such a procedure really does reduce the concentration of manganous chloride and cobalt chloride to extremely low values. The purified ether solution was irradiated with fast neutrons from the Berkeley cyclotron to form, among other things, very small amounts ($\sim 10^{-15}$ g.) of radio-manganese. This ether solution (volume, 82 cc.) was then shaken with two 13-cc. samples of triply-distilled 6 N hydrochloric acid, and great care was exercised to avoid contaminating the second hydrochloric acid extract with any of the first extract that may have escaped removal from the separatory funnel. From the behavior of manganese chloride in ordinary amounts, one would expect that 99.97% of the radio-manganese would appear in the first hydrochloric acid extract. To test this, the hydrochloric acid extracts were purified as follows, and their activity measured with a Geiger counter. Ferric chloride was removed from the two extracts by shaking with ether. Manganese chloride and monosodium hydrogen phosphate were added to each solution to serve as carriers for the subsequent precipitations and concentrated nitric acid was added to oxidize to phosphate any radio-phosphorus in the solution. (Radio-phosphorus and radio-chlorine were always present as a result of the action of neutrons on the chlorine originally present.) Phosphates were then removed by precipitation as $(NH_4)_3PO_4 \cdot 12MoO_3$ and manganese was recovered as $MnO(OH)_2$ by the action of sodium hydroxide and bromine water. A further purification of the $MnO(OH)_2$ was effected by dissolving it in an acidified solution of hydrogen peroxide and reprecipitating from concentrated nitric acid with potassium chlorate.

Results.—Measurements on the radioactivity of the two manganese samples showed that nearly all of the radio-manganese appeared in the first extract. Nevertheless, a very slight activity (0.7% of that in the first extract) appeared in the second extract, which was not to be expected from the extremely small distribution coefficient of manganese chloride between ether and 6 N hydrochloric acid (see below). It seems very probable, however, that traces of radio-silicon (half-life two and four-tenths hours) formed from the walls of the vessel may have entered the solution and been precipitated in part along with the manganese dioxide. Because of this uncertainty the conclusion to be drawn from this experiment is only qualitative. Thus, minute amounts of manganese chloride may be extracted from ether, at least qualitatively, in the same manner as manganese chloride in larger amounts.

It may be remarked, however, that the ether used to remove the ferric chloride from the first hydrochloric acid extract showed no detectable radio-manganese, a result to be expected if minute amounts behave in the same manner as larger amounts.

III. Distribution of $(NH_4)_2Co(SCN)_4$ between Water and Amyl Alcohol

Experimental Details.—Cobalt-free ammonium thiocyanate solution was prepared by shaking a 40% solution of the C. P. salt several times with doubly-distilled *s*-amyl alcohol. This procedure removed any cobalt which might be present, together with about half of the ammonium thiocyanate.

Cobalt-free iron was deposited in a thin film on a pure silver plate by electrolyzing (with a platinum anode and a silver cathode) a water solution of cobalt-free ferric chloride prepared as before. A scrupulously clean porous alundum cup prevented excessive diffusion of chlorine from the anode to the cathode. The film of iron so formed was bombarded in air with deuterons to form radio-cobalt with a half-life of eighteen hours, together with small amounts of radio-manganese, radio-iron, and long-lived radio-cobalt isotopes. The silver plate on which the iron was deposited also became strongly radioactive due to the formation of short-lived silver isotopes and due to the formation of a radio-cadmium isotope (half-life 7.2 ± 0.5 hrs.) heretofore observed only from the action of protons on silver. Part of the iron film was dissolved, after bombardment, with pure 6 *N* hydrochloric acid. The acid evidently reached the silver backing in places, for radio-cadmium, dissolved from the surface of the silver, was detected easily in all of the samples. To the solution of iron in hydrochloric acid, doubly-distilled (in Pyrex) 6 *N* nitric acid was added to oxidize ferrous iron, the solution was shaken with ether to remove the iron, evaporated to dryness, and taken up in ammonium thiocyanate solution prepared as described above. The distribution coefficient (between this solution and pure doubly-distilled *s*-amyl alcohol (b. p. 118.0 ± 0.5°) of the minute amounts of $(NH_4)_2Co(SCN)_4$ thus formed ($\sim 10^{-12}$ g.), was determined in substantially the same manner as that described above for gallium chloride. One difference lay in the fact that the two amyl alcohol extracts were finally shaken with dilute ammonium hydroxide solution which brought the radio-cobalt back into the aqueous layer. This was at once a convenience and a further test of the principle under consideration. In these extractions, of course, relatively large amounts of ammonium thiocyanate are transferred along with the ammonium cobaltothiocyanate.

Results.—The results so obtained are presented in Table II. Experiment 6 was identical with 5 except that ordinary pure iron, containing traces of cobalt, was used for the bombardment. Within the limits of the experimental error the results are the same, indicating again that very low concentrations of matter behave in partition processes like the same substances at ordinary concentrations.

TABLE II

DISTRIBUTION RATIO OF $(NH_4)_2Co(SCN)_4$ BETWEEN *s*-AMYL ALCOHOL AND AQUEOUS AMMONIUM THIOCYANATE SOLUTION

Expt.	Initial concn. of $CoCl_2$	Distribution ratio *K*
5	$\sim 10^{-12}$	10.9
6	$\sim 10^{-6}$	10.05

The samples obtained in experiment 5 were found to contain appreciable amounts of radio-cadmium (7.2 ± 0.5 hr.), and an approximate value for the distribution ratio of cadmium between *s*-amyl alcohol and ammonium thiocyanate solution was obtained ($K = 0.15$). Qualitative experiments with inactive cadmium salts in ordinary amounts showed a similar behavior.

The chemical identity of the seven and two-tenths-hour period here obtained was established by separating cadmium, manganese and cobalt from a new sample by adding carriers for the radio-elements and precipitating each in a conventional manner. The seven and two-tenths-hour period was found in the cadmium precipitate, and its radioactive properties were substantially the same as those reported by Ridenour, Delsasso, White and Sherr,[3] who produced this radioactive body by bombarding silver with protons.

IV. Distribution Ratios of Several Metallic Halides between Ether and Hydrochloric Acid

Since the hydrochloric acid used in the experiments listed in Table I had been shaken with ether several times, its quantitative composition was not accurately known. A series of experiments was performed in which the composition of the two phases could be easily and accurately reproduced. In these experiments the concentration of the substance whose distribution ratio was being measured was always small, but no effort was made to remove all traces of the element before the bombardment.

Experimental Details.—Hydrochloric acid of known concentration (standardized with anhydrous sodium carbonate) was shaken with an equal volume, at 20°, of dried ether. The heat of mixing was removed by cooling in a thermostat at 20°, and the two liquid phases were used at the compositions thus obtained. Experiments with gallium chloride were made in the manner already described except that traces of gallium originally present in the C. P. zinc chloride were not removed before bombardment. Measurements on ferric chloride were made in the presence of 0.01 *M* inactive iron. Experiment 14 with cobaltous chloride was made from a very active sample of long-lived radio-cobalt in which inactive cobalt was also present to the extent of about 10^{-7} mole per liter of solution. The ether and aqueous phases were evaporated and compared. Experiment 15 was carried out in the same manner with two and six-tenths-hour radio-manganese and the result checked by colorimetric experiments with inactive manganous chloride.

Results.—The results of these experiments are presented in Table III. The distribution ratio, *K*, for gallium chloride is seen to reach a maximum at about 5.5 *N* as originally reported by Swift.[4] His values do not agree very well with those in Table III, however, perhaps because his method of preparing the ether-saturated hydrochloric acid differed from that used in the present research. Experiments 12 and 13 were carried out in order to determine whether any marked

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(3) Ridenour, Delsasso, White and Sherr, *Phys. Rev.*, **53**, 770 (1938).

(4) Swift, THIS JOURNAL, **46**, 2375 (1924).

TABLE III

DISTRIBUTION RATIOS OF SEVERAL METALLIC HALIDES BETWEEN ETHER AND HYDROCHLORIC ACID AT 20°

Expt.	Subst.	Half-life	[HCl], *N*	*K*
7	$GaCl_3$	83 hr.	6.50	10.6
8	$GaCl_3$	83 hr.	6.00	35.8
9	$GaCl_3$	83 hr.	5.50	53.8
10	$GaCl_3$	83 hr.	5.00	52.2
11	$GaCl_3$	83 hr.	3.97	4.9
12	$FeCl_3$	47 da.	6.00	31
13	$FeCl_3$	47 da.	5.00	23
14	$CoCl_2$	Long	5.5	$\sim 10^{-4}$
15	$MnCl_2$	2.6 hr.	6.0	$\sim 10^{-4}$

difference existed between the distribution ratios of ferric and gallium chlorides. Although experimental difficulties rendered the results from ferric chloride rather uncertain, there appears to be a marked difference between the results obtained for the two trichlorides. The somewhat anomalous behavior of ferric chloride in distribution processes noted by Dodson, Forney and Swift[5] was observed in these experiments, and was taken into account in calculating the distribution coefficients given in Table III. No elements other than iron were found to display anomalous behavior of this sort.

The completeness with which cobaltous chloride and manganous chloride may be held in the aqueous layer during an extraction is shown by the results of experiments 14 and 15. The values of *K* obtained in these two experiments may be regarded as upper limits.

Discussion.—It has been shown at ordinary concentrations that the activity coefficient of an ion in aqueous solution is determined by the ionic strength of the solution surrounding it and not by its own particular concentration. The results presented in Tables I and II may be considered as experimental evidence supporting this proposition at extremely low concentrations, since the ionic strength was essentially the same at the two concentrations studied. In the ether phase, also, the activity must have remained proportional to the concentration at the lowest concentrations attained, a result to be attributed, no doubt, to the presence of a relatively large amount of hydrochloric acid dissolved in the ether.

A result of considerable interest was obtained during one of the experiments with radio-cobalt and radio-cadmium. When a hydrochloric acid solution containing traces of radio-cobalt and radio-cadmium together with inactive iron in relatively enormous concentration was shaken with ether, the iron was readily and almost completely removed. The ether extract, however, showed no detectable radioactivity, indicating that the ether in removing 10^8 times as much iron as there was cobalt or cadmium in the solution showed no tendency to carry with it the other components of the solution. As a means of separating certain pairs of substances, extraction processes are evidently much superior to ordinary precipitation processes.

During the course of the experiments with radio-gallium a radioactive substance of half-life roughly seven and one-half hours was observed in addition to the well-known sixty-eight-minute and eighty-three-hour gallium isotopes. A description of the radioactive properties of the seven and one-half-hour body will be published elsewhere, but it is desired to note here that its chemical identity was established by showing that the distribution ratio of its chloride between ether and hydrochloric acid was always the same as that observed under the same conditions for the other radioactive isotopes of gallium present at the same time. This constitutes very strong evidence that the seven and one-half-hour period is due to an isotope of gallium rather than to some impurity present in the bombarded zinc.

The facts here presented indicate that in certain cases extraction processes may be used to advantage in the separation and identification of artificially produced radioactive elements. The advantages of such methods over the more conventional precipitation processes are: (1) no "carrying down" of unsuspected radioelements in unpredictable ways; (2) high concentration of the radioactive substance in the evaporated extract, thus eliminating self-absorption of the radiation and changes in the physical properties of the sample on standing; (3) chemical identification of the radioactive element by its distribution ratio, particularly if other known radioactive isotopes of the element are present. Extraction processes employing ammonium thiocyanate and amyl alcohol are of less value because they are less specific in their action.

We are greatly indebted to Professor E. O. Lawrence of the Department of Physics and to the staff of the Radiation Laboratory for the preparation of the radioactive substances used in this research.

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(5) Dodson, Forney and Swift, THIS JOURNAL, 58, 2573 (1936).

Summary

1. The distribution of minute quantities (*ca.* $10^{-12} - 10^{-15}$ g.) of soluble substances between liquid phases is shown in the cases studied to be quantitatively the same as that observed for the same substances in ordinary small concentrations.

2. Distribution ratios of several metallic halides between ether and hydrochloric acid are determined at low concentrations by the use of radioactive substances.

3. It is shown that the technique here employed may be of use in separating and identifying artificially prepared radioactive substances without the use of a non-radioactive carrier.

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Infrared Absorption Studies. VII. Complex Formation Due to Hydrogen Bonding

BY A. M. BUSWELL, W. H. RODEBUSH AND M. F. ROY

In an earlier paper[1] a considerable discussion was given of the conditions under which hydrogen bonding might occur. It was observed that for a hydrogen atom to be capable of forming a "bond" it must be active to a degree (*i. e.*, ionizable in the proper solvents). Furthermore, a generalization due to Venkateswaran[2] was noted. This generalization is that the shift of the fundamental absorption band when hydrogen forms a bond is the greater, and the band itself is the broader, the more active the hydrogen. In order to test the generalizations above it seemed to be desirable to examine compounds containing hydrogen that lay at either extreme of the range of activity. The two which seemed best suited for this purpose are chloroform and hydrogen chloride.

Ether Hydrochloride.—The existence of the ether–hydrogen chloride complex has been known for a long time and it was formerly characterized by organic chemists as an oxonium compound. More recently it has been recognized that it must be in the nature of a hydrogen bonded complex

$$R_2O \longleftarrow HCl$$

Of course by analogy with ammonium compounds, it might be supposed to be ionic in character. Undoubtedly a solution of hydrogen chloride in ether does show some conductance but the amount of ionization cannot be appreciable in a solvent of low dielectric constant for ions of small radius, and no typical salt-like crystal is formed as is the case with ammonium chloride.

Recently a number of spectroscopic studies have tended to confirm the foregoing conclusions. Walkenstein and Syrkin[3] have noted the absence of the Raman lines of hydrogen chloride in ether solutions. West and Edwards[4] have reported the absence of the harmonic at 1.7 μ for hydrogen chloride in ether. Similarly, West and Arthur[5] found no Raman lines for hydrogen chloride in ether solution.

Gordy and Martin[6] have observed the infrared spectrum of hydrogen chloride in ether, dioxane, and ethyl acetate and have found a broad intense band around 4 μ which they attribute to hydrogen bonding between the hydrogen chloride and the solvent.

In the investigation just mentioned the substance to which the hydrogen chloride bonds is used as the solvent. Since the solubility of hydrogen chloride is not large, this procedure has the obvious disadvantage of introducing an excess of solvent and hence a heavy absorption due to C–H in the region of the H–Cl absorption. It is necessary to work with thin layers of solution and as a result it is not possible to make definite observations upon the H–Cl vibration.

In our work we have avoided the above difficulty by using long cells containing a dilute solution of hydrogen chloride and ether in carbon tetrachloride. By changing the concentration of both hydrogen chloride and ether it is possible to produce and observe marked changes in the degree of association between the two substances.

Experimental

An 0.08 molal solution of ether in carbon tetrachloride was saturated with hydrogen chloride under a pressure slightly greater than atmospheric.

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(1) Article No. VI of this series, THIS JOURNAL, **60**, 2444 (1938).

(2) C. S. Venkateswaran, *Proc. Indian Acad.*, **7**, 13 (1938).

(3) M. Walkenstein and J. K. Syrkin, *Nature*, **139**, 288 (1937).

(4) W. West and R. T. Edwards, *J. Chem. Phys.*, **5**, 18 (1937).

(5) W. West and P. Arthur, *ibid.*, **5**, 10 (1937).

(6) W. Gordy and P. C. Martin, *ibid.*, **5**, 1075 (1937).