

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO.]

ADSORPTION OF RADIUM BY BARIUM SULFATE.

BY FRANK E. E. GERMANN.

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The study of the laws of adsorption is usually restricted to those substances which adsorb appreciable masses of material. It is on this account that charcoal is used to such a large extent. The reason for this limitation is that our analytical methods cannot be used to detect the difference in concentration of a solution caused by adsorbents that are not very active. As a result, our knowledge of adsorption phenomena is restricted to a rather limited region.

The case of the adsorption of a radio-active substance by a solid is an exception to the usual type, as in this case we have methods of measurement available other than the usual analytical methods. In the case of the emanation method of the analysis of the radium content of a solution, it is a simple matter to obtain an accuracy of 2 to 5%, where the total radium content is much less than one part per billion.

If radium-free barium sulfate be added to a standard solution of radium barium chloride, a certain quantity of the radium will be adsorbed by the sulfate. After equilibrium has been established, the sulfate can be filtered off and the residual radium in the solution determined. We thus have an ideal method for the study of the laws of adsorption which is applicable to the adsorption of masses which lie far below the quantities which could be determined analytically. The accuracy of the method is all that could be desired.

The study of this particular case is of considerable importance in the commercial refining of radium. Commercial hydrochloric acid contains appreciable quantities of soluble sulfates, which must be precipitated by means of barium chloride before the acid is used to dissolve the carbonates carrying the radium. If the barium sulfate is allowed to settle and the clear acid decanted as used, it may happen at times that traces of the insoluble sulfate are carried over with the acid. The question then arises as to the possible harm that this could do in the extraction of the radium from the carbonate. If the acid-insoluble "tails" run high in radium, how much of this should be attributed to the presence of barium sulfate? It was with these problems in view that the following investigation was undertaken.

A solution of radium barium chloride in approximately *N* hydrochloric acid was made up, and, after standing for several days, was standardized, as far as the radium content was concerned, by means of 3 samples, sealed for a month. When the emanation had reached equilibrium, it was boiled off in the usual way and the radium content of the solution determined.

The average of these 3 determinations showed a radium content of 22.79 $\times 10^{-10}$ g. of radium per cc. of solution.

The barium sulfate was prepared by adding sulfuric acid to a dilute solution of pure barium chloride while boiling. Prepared under these conditions, the sulfate settled readily, and could easily be washed by decantation to rid the precipitate of the sulfuric acid. The barium sulfate was then filtered off, dried, and ignited in a muffle for several hours to remove any residual traces of acid. After cooling, it was pulverized in an agate mortar and passed through a 200-mesh sieve in order to have greater uniformity in the size of the particles.

Ten cc. of the standard radium solution was then diluted to 80 cc. and 0.05 g. of barium sulfate added. The mixture was then boiled for about 20 hours, under a reflux condenser. Experience showed that equilibrium is not reached in 10 hours, but that boiling longer than 18 hours produced no further change in the mass adsorbed. After the adsorption equilibrium had been established, the barium sulfate was filtered off and the solution sealed and set away for a month prior to the emanation determination. Similar runs were made on the same volume of standard solution with varying masses of barium sulfate. Making all the runs under similar conditions, the final volumes of the solutions at equilibrium were the same, and hence the conditions were comparable. The results are tabulated below. Ten cc. of standard solution was used in all experiments.

Expt.	BaSO ₄ . G.	Ra/cc. at equilb. $\times 10^{10}$. G.
1	0	21.86
2	0	23.62
3	0	22.89
4	0.05	18.55
5	0.10	15.08
6	0.10	15.15
7	0.20	8.45
8	0.20	10.48
9	0.30	5.86
10	0.40	3.97
11	0.50	2.70

In addition to the above experiments, one blank was made up with all of the reagents except the standard radium solution. No activity was obtained from this test run, which served as a guarantee that the substances used were all free from radium with the exception of the standard radium solution.

According to the experimental work of Kroeker¹ on adsorption, we may write

$$\left(dx = \lambda \frac{a-x}{v} dm \right) \quad (1)$$

¹ Kroeker, Thesis, *Berlin*, 1892.

where x represents the mass adsorbed, a the total mass initially dissolved, v the volume of the solution, m the mass of the adsorbent, and λ a constant. On integrating the above expression, we obtain the equation

$$\lambda = v/m \ln\left(\frac{a}{a-x}\right) \tag{2}$$

Since x represents the mass adsorbed, $(a-x)$ would represent the concentration of the solution after adsorption equilibrium had been established, provided the volume v be taken as unity. Under these conditions, let $(a-x)$ be designated by y . Our equation becomes

$$\begin{aligned} \lambda &= 1/m \ln a/y \text{ or} \\ \ln y &= -m \lambda + \ln a \end{aligned} \tag{3}$$

which, written in the exponential form would be

$$y = a e^{-m\lambda} \tag{4}$$

According to Equation 3 it is evident that any case of true adsorption would give us a straight line curve if we plot $\log y$ as ordinates against mass m as abscissas. Curve I shows this to be the case.

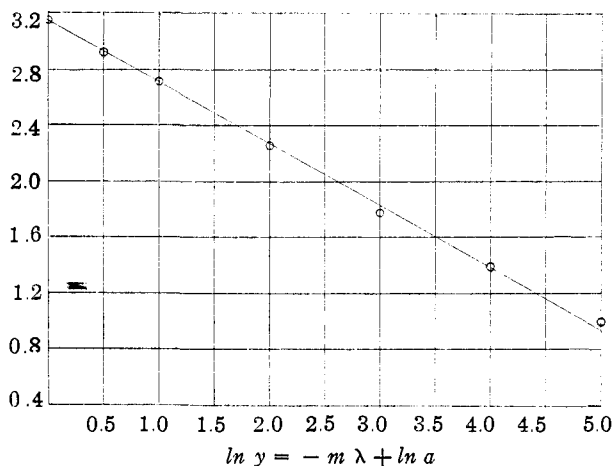


Fig. 1.

If we admit with Freundlich² that

$$\lambda = v/m \ln \frac{a}{a-x} = \alpha \left(\frac{a}{a-x}\right)^{-1/n} \tag{5}$$

in which α and n are constants depending only on the temperature and the nature of the dissolved substance, it can be shown that the usual form of the adsorption isotherm

$$x/m = \beta c^{1/p} = \beta \left(\frac{a-x}{v}\right)^{1/p} \tag{6}$$

² Freundlich, *Z. physik. Chem.*, 57, 395 (1906).

can be derived from 5 by expanding the two sides of the equation in series and neglecting all but the first term of each series. The term c is the concentration of the solution at equilibrium. Writing Equation 6 in the logarithm form, we obtain

$$\ln x/m = 1/p \ln c + \ln \beta \quad (7)$$

which shows that if we plot the logarithms of the ratio of the mass adsorbed to the adsorbing mass ($\log x/m$) against the logarithm of the equilibrium concentration, we should have a straight line. Curve II shows that this is borne out by experiment.

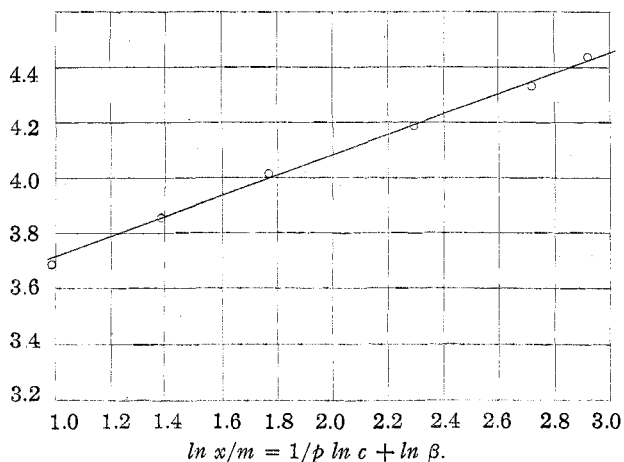


Fig. 2.

The usual procedure in adsorption work has been to use some such substance as blood charcoal, which adsorbs large quantities of material. Thus, in one set of experiments due to Freundlich, acetic acid and blood charcoal being used, the concentration of acid varied from 0.02 to 2.80 N , while the mass adsorbed per gram of charcoal varied between 0.028 and 0.226 g. In the experiments recorded in the present article, we are dealing with altogether different orders of magnitude. The concentration of radium chloride adsorbed per gram of adsorbent (BaSO_4) was of the order of 5×10^{-8} . No doubt the barium chloride was also being adsorbed, but this would be of no consequence as far as the radium adsorption is concerned. It thus appears that the same laws of adsorption apply to these minute quantities of radium that apply to the adsorption of ponderable masses of ordinary chemical substances.

When a radium barium chloride solution is incompletely precipitated by means of a soluble sulfate, such as sulfuric acid, the radium and barium come down in about the same proportion as they exist in the original solution, there being a slight concentration of the radium in the precipi-

tate. In other words, very little concentration of radium can be effected by a fractional precipitation method. Since the solubility of pure radium sulfate in water is so great that there could be no thought of a precipitation in the case of concentrations met with in the working up of radium ores, we are in the habit of speaking of the phenomenon of barium and radium precipitating together as adsorption. Looking at the question from the point of view of solubility product considerations, we could about as well explain the precipitation of the radium from the point of view of a salting out process which is brought about by the great excess of sulfate ions belonging to the dissolved barium. The fact that the adsorption law is followed in the case of the radium chloride would lead one to favor the adsorption theory in the case of a precipitation of the sulfate.

If we admit the validity of the adsorption theory in the case of a precipitation, the question arises as to why we can get a complete extraction of radium by means of a complete barium precipitation, whereas in the case of barium radium chloride in contact with barium sulfate we have an equilibrium radically different from what would be expected on the basis of the barium in solution compared to the barium present as sulfate. Thus 10 cc. of the standard solution contained about 0.04 g. of barium chloride. This solution, in contact with 0.05 g. of barium sulfate (of almost the same molecular weight as the radium sulfate) came to equilibrium with $\frac{4}{5}$ of the radium adsorbed on 0.04 g. or about half of the barium. Again 0.04 g. of barium chloride in the solution in equilibrium with 0.5 g. of barium sulfate came to equilibrium with $\frac{1}{7}$ of the radium adsorbed on $\frac{1}{12}$ of the barium. Evidently this is something more than just a proportionate distribution of the radium with the barium.

A better understanding of these phenomena can be obtained if we consider for a moment the adsorption equation as modified by Freundlich.

$$x/m = \alpha c^{1/n} \tag{8}$$

where x and m have the same significance as before and c is the concentration at equilibrium, or $\frac{a-x}{v}$. The term m represents the mass of the adsorbent, and is used as a measure of the surface area of the adsorbent, to which it bears a definite relation, in the case of an adsorbent of given fineness. Hence the term x/m is in a way a measure of mass adsorbed per unit area of adsorbent. The constants α and n are as mentioned above dependent only on the temperature and the nature of the dissolved substance. When we mix barium sulfate with a solution of barium radium chloride of known concentration, the area of the adsorbent is comparatively small. Since the concentration c is small and the area is small, the term x or the mass adsorbed will be finite. If on the other hand we precipitate barium sulfate from a solution of barium radium chloride, the area of

the adsorbent is tremendous, as the precipitate grows from about molecular dimensions. When the area becomes very large, x must also become large in order to keep c finite. The result is a complete precipitation of the radium with the barium. If these considerations are valid, we might expect to be able to precipitate all of the radium before all of the barium has been thrown down. In other words we might expect to be able to carry on a fractional precipitation. This does not seem to be the case with radium, but it may be noted that it can be done with certain radio-active substances.³ In this connection it is well to remember that adsorption is a specific property, depending not only on the adsorbent and the adsorbed substance, but also on the solvent.

We may make the above considerations clear by means of the following crude calculations. Let us assume that the diameter of the molecule is of the order of 10^{-8} cm. Its area, assuming it to be spherical, would be about 3×10^{-16} sq. cm. There would be approximately 10^{24} molecules per cc. of substance if we can assume close packing. Hence 1 cc. of solid substance of molecular sized particles would present an area of $10^{24} \times 3 \times 10^{-16}$, or 3×10^8 sq. cm.

Now suppose we take the precipitated barium sulfate which was put through a 200-mesh sieve. Assuming the wire to have the same diameter as the hole, we would have holes 0.006 cm. square. Particles smaller than this also pass through. Let us therefore suppose, for the sake of argument, that the average particle passing through has a diameter of 0.002 cm. Its radius will be 0.001 cm., and its area approximately 10^{-5} sq. cm. Of these particles there would be about 10^8 per cc. of solid substance, giving us a total area of $10^8 \times 10^{-5}$, or 10^3 sq. cm. We thus see that we have 1000 sq. cm. in the latter case as compared to three hundred million in the former. The former is three hundred thousand times the latter.

Regarding Equation 7 in the light of these figures we can readily see that x must approach as a limiting value the total mass of substance dissolved which is capable of being adsorbed. As the area of the adsorbent (a number proportional to m in the general case) becomes very large, the concentration c must approach zero.

Summary.

1. The adsorption law of Kroecker has been experimentally tested in the case of a radio-active substance and found to hold true.
2. The adsorption law of Freundlich has been experimentally tested and found to hold true in the case of a radio-active substance.
3. The same laws of adsorption which apply to the adsorption of ponderable masses are found to apply with an equal degree of accuracy to masses of 5×10^{-8} g. adsorbed per gram of adsorbent.

³ Unpublished work of the author.

4. The relationship existing between adsorption taking place during precipitation, and that taking place on a solid precipitate of definite surface area has been discussed.

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

THE SURFACE TENSIONS AND DENSITIES OF LIQUID MERCURY, CADMIUM, ZINC, LEAD, TIN AND BISMUTH.

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The purpose of this investigation was to secure data for the examination of metallic solutions from the standpoint of the theory of solubility which has been outlined by Hildebrand and extensively applied by him and his co-workers² to non-metallic solutions. Although surface tension has proved to be a criterion of great value with non-metallic solutions, the evident inaccuracy of much of the data heretofore published upon the surface tensions of liquid metals has made the work herein described prerequisite to the accomplishment of the above purpose.

The method selected for our purpose is one originated by Cantor³ and extensively applied by Jaeger⁴ to non-metallic liquids. The method as it is generally employed consists in determining the pressure necessary to force a bubble of inert gas from the end of a sharp edged platinum capillary immersed in the liquid. On account of the impossibility of using a metallic capillary with liquid metals the process has been reversed in the present work so as to measure the pressure necessary to force a tiny drop from the tip of a quartz capillary directed upwards. The theory of this method is as follows.

The free surface energy of a sphere of liquid of surface s and surface tension γ is γs . If the drop is increased infinitesimally in size by introducing more liquid, say, through a fine capillary, the work done against the surface tension is γds . This is equal to the pressure exerted by the tension upon the interior of the drop multiplied by the increase in volume dv , so that γds equals $p dv$. Since $s = 4\pi r^2$ and $v = \frac{4}{3}\pi r^3$, we have $\gamma = pr/2$.

If we have a small capillary of radius a and apply pressure to force out a drop of the liquid, the radius of curvature of the drop will gradually

¹ Thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **43**, 500 (1921). Hildebrand and Jenks, *ibid.*, **42**, 2180 (1920). Hildebrand and Buehrer, *ibid.*, **42**, 2213 (1920).

³ Cantor, *Wied. Ann.*, **47**, 399 (1892).

⁴ Jaeger, *Z. anorg. Chem.*, **101**, 1 (1917).