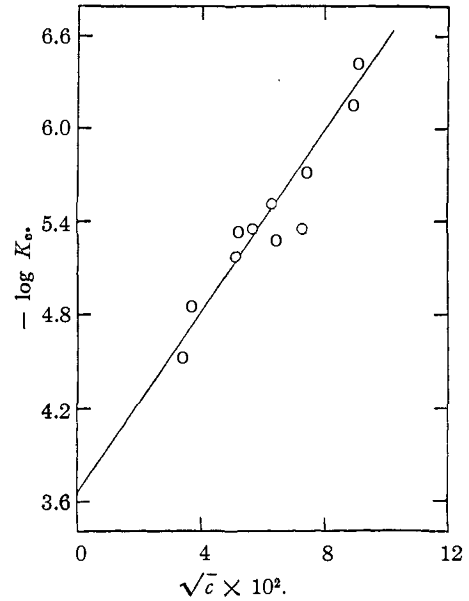

Fig. 8.—Variation of $-\log K_c$ for the reaction $C_8H_{11}NH^+ + Cl^- \rightleftharpoons C_8H_{11}N + HCl$ with concentration of dimethylanilinium ions.

$-\log K_c$ *versus* $\sqrt{c}$ given in Fig. 8, where c is the concentration of dimethylanilinium ions calculated from the spectral data, yielded a value of $K_a = 2 \times 10^{-4}$ and a value of $k = 14$. Other authors have reported low values of k for solvents of low dielectric constant from conductance measurements. In this instance the low value appears to be due in part to the presence of a large number of $C_8H_{11}NH^+ \text{--} Cl^-$ ion pairs, which reduces the ionic strength below the calculated value.

Summary

Electric moments have been determined for sulfur dioxide, tri-*n*-butylamine, trimethylamine–sulfur dioxide, triethylamine–sulfur trioxide and tri-*n*-butylamine–sulfur trioxide. The N → S bond moments in these addition compounds have been evaluated.

Dissociation constants have been calculated for trimethylamine–sulfur dioxide and dimethylaniline hydrochloride in chloroform from ultraviolet absorption measurements, and for the sulfur dioxide addition compounds of pyridine, triethylamine, and tri-*n*-butylamine in benzene from dielectric constant and density measurements. Both absorption and dielectric constant measurements reveal that the order of decreasing stability of the sulfur dioxide addition compounds is trimethylamine > triethylamine > tri-*n*-butylamine > pyridine. The sulfur trioxide addition compounds of trimethylamine and triethylamine appear to be undissociated in benzene and chloroform solutions.

Interaction of trialkylamines with sulfur dioxide results in a very large increase in absorption in the 270 mμ region. The addition compounds of sulfur trioxide with trialkylamines are transparent in this region. Sulfur trioxide shows an effect similar to that of the proton in altering the spectra of pyridine and dimethylaniline.

NOTRE DAME, INDIANA RECEIVED JULY 12, 1948

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

Rate of Adsorption of Barium Ions in Extreme Dilution, by Hydrous Ferric Oxide

BY M. H. KURBATOV

Introduction

In earlier work it was realized that the extent of adsorption of divalent ions from very dilute solutions on hydrous ferric oxide depended not only on the usually recognized factors of temperature, *p*H, amount of adsorbent, volume and salt concentration but also on the duration of adsorption. It was observed that adsorption was not discontinued with the separation of the solid adsorbent, but that when the co-precipitation procedure was used in the case of very dilute solutions, there was an observable adsorption rate. Particularly was this true when the amount of adsorbate was less than 10^{-6} gram atom, the volume of solution of the order of 10–30 ml. and the quantity of adsorbent 1 or 2×10^{-5} gram atom of iron, the effect being more pronounced with decreased amounts of adsorbate. From this observation there arose the possibility of determining a rate of ion adsorption from solution.

Procedure

The adsorption procedure and the preparation of barium 133 as carrier-free tracer are described in a previously published paper.[1] For the rate studies, 2×10^{-5} gram mole ferric chloride was mixed with the chosen quantity of stable barium chloride and tracer, all in acid solution, and the mixture titrated rapidly with ammonium hydroxide to the selected *p*H. Thus, the so-called co-precipitation procedure, in which hydrous ferric oxide was precipitated in the presence of barium ions, was used. Some barium was adsorbed during titration in the *p*H interval from the formation of the solid phase to the selected *p*H of a particular series of experiments, the amount adsorbed during titration increasing with *p*H (see Table II).

The co-precipitation procedure has some advantage over the "real" adsorption procedure (in

[1] M. H. Kurbatov, Fu-Chun Yu and J. D. Kurbatov, *J. Chem. Phys.*, **16**, 87 (1948).

which latter case barium ions in solution are added to a solution containing the previously precipitated hydrous ferric oxide) in that the selected conditions such as salt concentration, volume of liquid phase, etc., are more reproducible and these conditions are of significance in the rate of adsorption in this liquid–solid system.

The time intervals at which adsorption was measured were from one to several hours; the zero time being taken as that at which the final *p*H was reached. Each determination was made on a separate sample, the rate of adsorption being found from a series of samples, initially prepared, under experimentally identical conditions.

Experimental

Rate of Adsorption of Barium Ions in Concentrations of 3×10^{-6} and 3×10^{-10} Gram Atom per Liter.—In studies of adsorption isotherms it has been established that the fraction of barium adsorbed (under specified conditions) in a given time interval of, for instance, one, two or four hours, increases with dilution down to a concentration of 10^{-8} gram atom per liter. Below this concentration the fraction adsorbed becomes experimentally constant for the given time interval.[2]

Therefore, it is possible to study the rate of adsorption after titration is completed in concentration ranges in which the fraction adsorbed is either independent or not independent of the changing concentration. To exemplify these two conditions and to observe the variation in rate due to concentration, the barium quantities selected were 1×10^{-11} gram atom and 1×10^{-7} gram atom per 32 ml. of liquid phase. The results are given in Table I.

TABLE I

RATE OF ADSORPTION OF BARIUM ION ON HYDROUS FERRIC OXIDE

Constant factors: *p*H, 8.00 ± 0.01; temp., 25° ± 1°; Fe, 2×10^{-5} g. at., vol. of sol. 31.98 ± 0.02 ml., NH_4Cl concn., 3.5×10^{-2} *N*; Ba = 1×10^{-7} g. at.

Adsorp. period, hr.	Activity in sol., counts/min.	Tracer, counts/min.	Ba adsorbed, g. at. × 10^8
1.0	916	1110	1.80
2.1	868	1095	2.05
4.0	784	1020	2.32
7.0	828	1120	2.62
20.1	724	1065	3.21
41.2	381	610	3.75
65.8	746	1213	3.85
99.9	422	702	4.00
122.2	227	374	3.93
Vol. of soln., 32.00 ± 0.05 ml. Ba = 1×10^{-11} g. at.			
			g. at. × 10^{12}
1.0	833	1075	2.26
2.2	800	1085	2.63
4.0	759	1090	3.04
10.1	670	1070	3.75
20.2	559	1070	4.78
42.8	316	688	5.40
67.7	547	1190	5.47
100.3	323	707	5.43
126.5	218	470	5.54

It can be seen that in equal time intervals the fraction of barium adsorbed is higher for the lower concentration in agreement with the previous isotherm studies. Also the rate of change with time of the fraction of barium adsorbed is greater for the lower concentration.

After sixty hours the quantity of adsorbed barium, within the limits of experimental observation, remains constant for both concentrations.

The Dependence of Rate of Adsorption on Hydrogen Ion and Ammonium Chloride Concentrations.—The procedure used in securing the data in Tables II, III, and IV differed from that used in obtaining the data in Table I in that the volume of liquid phase (∽32 ml. initially) decreased at each successive measurement. That is, the five determinations of barium adsorbed at a given *p*H and salt concentration in the time interval from 0.5 to 30, 50 and 45 hours, respectively, were obtained by successive removals

TABLE II

CHANGE IN ADSORPTION WITH TIME AND REMOVAL OF PORTIONS OF SOLUTION

NH_4Cl concentration 3.8×10^{-3}*N*; constant factors: temp., 25° ± 1; total Ba, 1×10^{-11} g. at.; Fe, 2×10^{-5} g. at.; vol. of sol., 32.6 ± 0.5 ml.

Adsorp. period (from time titrated), hours	Activity in 5 ml. sol. removed, counts/min.	Tracer, counts/min.	Ba adsorbed, g. at. × 10^{12}	Total Ba present at each time, g. at. × 10^{12}
		*p*H 9.02		
0.5	84	2100	7.38	10.00
5.0	62	2035	7.97	9.60
10.0	33	1595	8.44	9.31
20.0	20	1395	8.66	9.12
30.0	14	1258	8.73	8.99
		*p*H 8.66		
0.5	130	2120	5.95	10.00
5.0	95	2000	6.80	9.39
10.0	54	1540	7.47	8.94
20.0	32	1325	7.90	8.61
30.0	26	1175	7.92	8.40
		*p*H 8.00		
0.5	231	2160	3.15	10.00
5.0	199	1921	3.90	8.97
10.0	135	1383	4.55	8.00
20.0	115	1118	4.68	7.22
30.0	91	732	4.53	6.48
		*p*H 7.60		
0.5	283	2165	1.50	10.00
5.0	266	1884	1.95	8.69
10.0	204	1294	2.15	7.46
20.0	175	983	2.35	6.28
30.0	121	581	2.46	5.16

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[2] M. H. Kurbatov and J. D. Kurbatov, THIS JOURNAL, **69**, 438 (1947).

TABLE III

CHANGE IN ADSORPTION WITH TIME AND REMOVAL OF PORTIONS OF SOLUTION

NH_4Cl concentration $3.3 \times 10^{-2}N$; constant factors: temp., 25 ± 1°; total Ba, 1×10^{-11} g. at.; Fe, 2×10^{-5} g. at; vol. of sol., 33.1 ± 0.4 ml.

Adsorp. period (from time titrated), hours	Activity in 5 ml. sol. removed, counts/min.	Tracer counts/min.	Ba adsorbed, g. at. $\times 10^{12}$	Total Ba present at each time, g. at. $\times 10^{12}$
		*p*H 8.99		
0.5	101	2050	6.74	10.00
5.0	78	1950	7.36	9.51
20.0	40.6	1418	7.92	9.13
30.0	20.4	962	8.19	8.87
50.0	12.0	842	8.36	8.68
		*p*H 8.51		
0.5	179	2055	4.30	10.00
5.0	147	1880	5.18	9.13
20.0	90	1273	5.58	8.22
30.0	46	852	6.20	7.67
50.0	31.5	699	6.42	7.26
		*p*H 8.13		
0.5	244	2070	2.25	10.00
5.0	198	1835	3.39	8.82
20.0	123	1235	4.28	7.87
30.0	79	795	4.50	7.09
50.0	60.5	612	4.76	6.38
		*p*H 7.68		
0.5	306	2110	0.47	10.00
5.0	276	1785	1.20	8.54
20.0	175	1128	2.11	7.22
30.0	112.5	672	2.46	6.10
50.0	106.5	485	2.71	5.08

TABLE IV

CHANGE IN ADSORPTION WITH TIME AND REMOVAL OF PORTIONS OF SOLUTION

NH_4Cl concentration $3.0 \times 10^{-1}N$; constant factors: temp., 25 ± 1°; total Ba, 1×10^{-11} g. at; Fe, 2×10^{-5} g. at; vol. of sol., 34.1 ± 0.6 ml.

Adsorp. period (from time titrated), hours	Activity in 5 ml. soln. removed, counts/min.	Tracer counts/min.	Ba adsorbed, g. at. $\times 10^{12}$	Total Ba present at each time, g. at. $\times 10^{12}$
		*p*H 9.1		
0.5	154	1475	2.73	10.0
5.0	121	1334	4.11	8.95
15.0	116	1332	4.61	8.13
25.0	61.3	827	5.24	7.42
45.0	53	682	5.28	6.86
		*p*H 8.5		
0.5	182	1470	1.65	10.0
5.0	168	1284	2.19	8.76
15.0	159	1254	3.06	7.62
25.0	109	732	2.95	6.63
45.0	86	559	3.28	5.64
		*p*H 8.02		
0.5	288	2025	0.30	10.0
5.0	200	1350	1.18	8.58
15.0	196	1184	1.46	7.31
25.0	132	674	1.53	6.10
45.0	121	477	1.38	4.91
		*p*H 7.50		
0.5	297	2035	0	10.0
5.0	235	1350	0	8.51
15.0	219	1138	0.66	7.02
25.0	159.5	634	0.39	5.66
45.0	139	417	0.40	4.07

of portions of solution from one original sample. This procedure so reduced the number of individual samples as to allow simultaneous study of several different hydrogen ion concentrations and salt concentrations. The main distinction between Tables II, III and IV is the ammonium chloride concentration, 3.8×10^{-3}, 3.3×10^{-2} and 3.0×10^{-1} *N*, respectively.

These experiments even though they involved repeated removals of the liquid phase resulted in a continued increase in adsorption in consecutive periods.

From Table II (3.8×10^{-3} *N* NH_4Cl) it may be seen that the rate of change of adsorbed barium increases as the *p*H increases from *p*H 7.6 to 8.7 but then the rate drops off at *p*H 9.0.

A similar though not so marked trend may be seen in Table III (3.3×10^{-2} *N* NH_4Cl). The change in the amount adsorbed between 0.5 and 30.0 hours increases with *p*H from *p*H 7.7 to 8.1 but then appears to decrease as the *p*H is increased farther. In the experiments represented in Table IV the salt concentration was 3×10^{-1} *N* and the tracer measurements consequently less accurate. However, the data show similar trends to those in Tables II and III.

If Tables II, III and IV are compared (recognizing the more approximate nature of the data in Table IV) using the change in the amount adsorbed from 0.5 to 25 or 30 hours at similar *p*H values it can be seen that:

(a) At *p*H 9, changing the ammonium chloride concentration from 3.8×10^{-3} to 3.0×10^{-1} *N* has no significant effect on the rate of adsorption after titration although the amount adsorbed initially (during titration) is decreased by increased salt.

(b) At *p*H 8.5 or 8.6 there is little difference in the effect of 3.8×10^{-3} and 3.3×10^{-2} *N* salt on the rate.

(c) At *p*H 8 and 7.5 the change in adsorption with time is increased as the salt concentration is increased from 3.8×10^{-3} to 3.3×10^{-2} *N*.

(d) The difference in the rate referred to in (c) results largely from decreased initial adsorption with increased salt, the total adsorption after 30 hours being essentially the same for 3.8×10^{-3} *N* or 3.3×10^{-2} *N* salt at approximately *p*H 7.5 or 8.

The following data selected from Tables II and III show the direction and greatest observed extent of the effects of salt and hydrogen ion concentration on rate of adsorption (after titration)

(H^+)	NH_4Cl concn., *N*	Change in g. at. Ba adsorbed in interval from 0.5 to 30 hours after titration × 10^{12}
2.5×10^{-8}	3.8×10^{-3}	$2.46 - 1.50 = 0.96$
2.7×10^{-9}	3.8×10^{-3}	$7.92 - 5.95 = 1.97$
2.1×10^{-8}	3.3×10^{-2}	$2.46 - 0.47 = 1.99$

Discussion of Results

It has been established that, in spite of extreme dilution (1×10^{-11} gram atom of Ba per 32 ml.) barium is not completely adsorbed by 2×10^{-5} gram atom of hydrous ferric oxide under the conditions used though this quantity of adsorbent can remove 4×10^{-8} gram atom barium from a solution originally containing 1×10^{-7} gram atom barium, other conditions being comparable. The maximum adsorption observed for the two above quantities of barium was 54 and 39%, respectively, and was obtained within forty to sixty hours.

It has also been found that the *p*H of the solution and salt concentration not only affect the initial amount of adsorption (from a solution containing 1×10^{-11} gram atom barium), but affect the rates as well. In the interval from *p*H 7.5 to 8.0 or 8.5 the rate (after the initial adsorption) increases with decrease in hydrogen ion concentration and the quantity adsorbed, at any given time interval, increases with decreased hydrogen ion concentration. In the range of ammonium chloride concentrations from 3.8×10^{-3} to 3×10^{-2} *N* the rate (after the initial adsorption) increases with increase in salt concentration where the *p*H is 7.5 or 8.0 although the quantity adsorbed at any given time decreases with increased salt concentration.

In considering these rate studies several possible mechanisms suggest themselves as rate-determining processes.

Since the adsorption system used involves initial mixing followed by rapid settling of the solid phase and no further stirring, ionic diffusion through solution might be considered as the rate-determining process after settling. However, if the usual equation for diffusion of ions through solution to a solid electrode is applied the fraction left in solution is found to decrease from 83 to 1% in 100 hours while experimentally it decreases from 82% to only 60% in that time. The equation indicates as much adsorption in four hours as is observed in 100 hours.

Diffusion in and through solid particles[3] has similarly been ruled out as the major process since that equation contains a constant ratio[4] which when evaluated from the above data is not constant but varies from a value of 0.19 at $t = 1$ to 0.07 at $t = 10$.

The adsorption of divalent cations may be considered as competitive[1] with adsorption of monovalent cations, $H^+ + NH_4^+$. To treat this more specifically an ionic displacement reaction can be written as

$$Ba^{++} + S_2Ad \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2S^+ + BaAd$$

in which Ba^{++} represents the moles of Ba^{++} in solution, S_2Ad represents the adsorbent with H^+ and/or NH_4^+ ions adsorbed, S^+ represents H^+ and/or NH_4^+ in the solution and BaAd the adsorbent with adsorbed barium. It is not intended to imply here that H^+ and NH_4^+ ion effects are directly additive, nor of magnitude proportional to their concentrations, but the effect of both, though they may be competitive with each other, is assumed to be in opposite direction to that of the divalent ion.

In the systems studied experimentally the initial Ba^{++} concentrations were 3×10^{-6} and 3×10^{-10} gram atom per liter (1×10^{-7} and 1×10^{-11} g. at. per 32 ml.) while the salt concentration was 10^{-2} *N* and the H^+ concentration 10^{-8} *N*.

It may be postulated that in the initial rapid adsorption—the rate of which has not been measured because of changing conditions—both monovalent and divalent ions are adsorbed and that the slow measured rate represents the subsequent desorption of monovalent ions and preferential adsorption of divalent ions.

The rate of formation of BaAd would then be

$$\mathrm{d}[BaAd]/\mathrm{d}t = k_1[Ba^{++}][S_2Ad] - k_2[S^+]^2[BaAd]$$

which may be rewritten in the form

$$\mathrm{d}[BaAd]/\mathrm{d}t = -[BaAd](k_1[Ba^{++}] + k_2[S^+]^2) + k_1[Ba^{++}G]$$

in which G is a constant equal to the sum of S_2Ad and BaAd.

It has been shown experimentally[2] that the fraction of barium adsorbed is independent of the original concentration if the latter is below 10^{-7} gram atom per liter so the *effect* of the Ba^{++} concentration in solution can be considered constant for the lower concentration of barium used in the rate studies (*i. e.*, 3×10^{-10} g. at./liter). With an initial salt concentration of the order of 10^{-2} *N* any H^+ or NH_4^+ ion desorbed (being of the order of magnitude of 10^{-10}) would represent a negligible change in S^+ concentration during its desorption.

Therefore $k_1[Ba^{++}] + k_2[S^+]^2$ can be considered as a constant D and the equation can be simplified to

$$\mathrm{d}[BaAd]/\mathrm{d}t = -[DBaAd] + k_1[Ba^{++}G]$$

which on integration gives

$$[BaAd] = \frac{k_1[Ba^{++}G]}{(k_1[Ba^{++}] + k_2[S^+]^2)}[1 - Ke^{-Dt}] \qquad (1)$$

If the value of [BaAd] is Q at t, is Q_0 at t_0 and is Q_∞ at t_∞ then Equation (1) can be shortened to

$$Q = Q_\infty - Ke^{-Dt}Q_\infty$$

and if the fraction of Ba adsorbed at $t = Q/Q_\infty = F$ and at $t_0 = Q_0/Q_\infty = F_0$ the expression becomes

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(3) C. E. Boyd, A. W. Adamson and L. S. Myers, Jr., THIS JOURNAL, **69**, 2836 (1947).

(4) $D^1\pi^2/r_0^2$ in which D^1 is diffusion coefficient in the solid and r_0 the radius of solid particles.

$$\log (1 - F) = \frac{-D}{2.303} t + \log (1 - F_0) \qquad \text{(1a)}$$

$(1 - F_0)$ being constant for any given set of conditions.

This equation indicates that a straight line should result from a plot of log $(1 - F)$ against t when the conditions assumed in the derivation are met. Accordingly it was found that the rate of adsorption of barium from the lower concentration studied gives the straight semi log plot while the higher concentration does not give a straight line (Fig. 1).

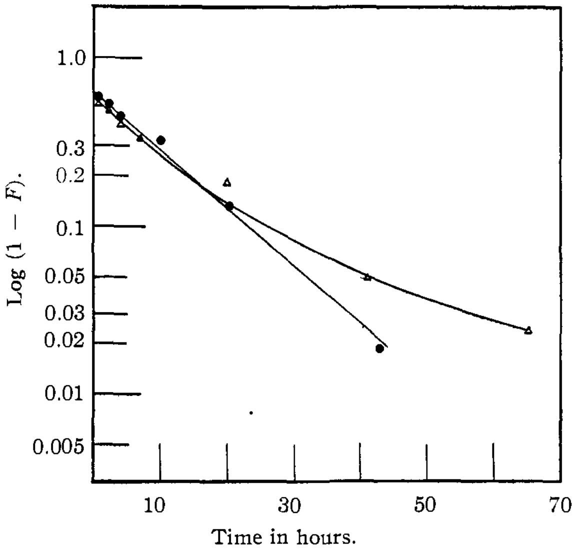

Fig. 1.—Adsorption of barium on hydrous ferric oxide represented as ion exchange rate: O, Ba = 1×10^{-11} g. at.; △, Ba = 1×10^{-7} g. at.; pH = 8.00 ± 0.01; Fe = 2×10^{-5} g. at.; vol. = 32.00 ± 0.05 ml.; NH_4Cl = 3.5×10^{-2} N.

Although this equation is essentially the same as the equation for diffusion through a thin liquid film[3] the displacement mechanism is favored because the equation based on displacement shows several relations which are compatible with previous experimental observations. Some of these are:

(1) The fraction of barium adsorbed at any given time with a constant quantity of adsorbent is independent of total barium when the concentration of Ba^{++} used is less than 10^{-7} g at./liter with a salt concentration of 6×10^{-3} N. When this is true the ratio of adsorbed barium to barium left in solution is also constant. Equation (1) indicates that $[BaAd]/[Ba^{++}]$ is dependent upon the sum of $k_1[Ba^{++}]$ and $k_2[S^+]^2$. If $k_1[Ba^{++}]$ is insignificant as compared to $k_2[S^+]^2$ the fraction $[BaAd]/[Ba^{++}]$ is independent of Ba^{++} concentration but when $k_1[Ba^{++}]$ becomes significant when added to $k_2[S^+]^2$ the fraction $[BaAd]/[Ba^{++}]$ not only changes but decreases as has been observed.

(2) The fraction $[BaAd]/[Ba^{++}]$ (at constant time) decreases as salt or hydrogen ion concentration (S^+) increases which is consistent with the $[S^+]^2$ factor being in the denominator of equation (1).

(3) The quantity adsorbed from a given concentration of barium (at constant time) increases with increased quantities of hydrous ferric oxide. This is consistent with the G factor being in the numerator of equation (1).

(4) The rate of change with time of the quantity of barium adsorbed under the conditions described above increases with increased salt concentration. Increase in S^+ should decrease the rate if K were constant for all conditions but it is not. K which is $(1 - F_0)$ increases with salt concentration in such a manner as to more than balance the effect of increased S^{+2}.

(5) An increase in hydrogen ion concentration from pH 8.5 or 8.0 to pH 7.6 (other factors being constant) decreases the rate after the initial coagulation. This is in accord with the equation if the change in K is neglected. Actually, K increases in value with increased hydrogen ion concentration but the change (in the case of 3.8×10^{-3} salt) may be approximated as from 0.25 to 0.40 for a change from pH 8.6 to 7.6 while a change from 3.8×10^{-3} N to 3.3×10^{-2} N NH_4Cl at pH 7.6 results in a change of K from 0.40 to 0.83.

In conclusion it may be said that while the observed rate of attachment of barium ions to hydrous ferric oxide after the initial co-precipitation adsorption may involve more than one mechanism the rate for very dilute solutions is well expressed by a simple chemical equilibrium. The equation derived on this basis is consistent with both current and previous observations on the effect of salt, hydrogen ion concentration and quantity of adsorbent on quantities adsorbed at constant time and on rate of adsorption.

Acknowledgment.—It is a pleasure to express thanks to Prof. Edward Mack, Jr., whose stimulating support of nuculear chemistry research made this work possible.

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Summary

The rate of adsorption of barium ions has been studied with the purpose of selecting optimum conditions for carrier-free target chemistry relative to the nuclear reactions $Cs(dn)Ba^{133}$ and $Cs(d2n)Ba.^{134}$

At a concentration of barium ions of 3×10^{-10} gram atom per liter with 1×10^{-5} gram mole of hydrous ferric oxide as adsorbent, other conditions being as described, the rate of adsorption was observed in an interval from one to 100 hours. It was found that in spite of the extreme dilution of barium its adsorption did not proceed to complete removal of the divalent ions from solution but reached its highest value within forty to sixty hours.

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.

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[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.

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