atom is unable to stay far enough away from all of the phenyl groups.

Whereas these direct calorimetric measurements are inaccurate because of accompanying oxidation, it should be emphasized that indirect calculations obtained from combustion measurements are still less reliable. The latter values are differences of large quantities which are themselves uncertain because it is difficult to be sure of the products of combustion of halogen compounds.

The authors are glad to acknowledge the support of this investigation by the Wisconsin Alumni Research Foundation.

Summary

1. The photo-kinetics of bromine substitution and addition have been studied for carbon tetrachloride solutions of toluene, diphenylmethane, triphenylmethane and cinnamic acid, making use of calorimetric measurements.

2. All these brominations, carried out in blue light (4360 Å.), are chain reactions and all are inhibited by oxygen.

3. All the quantum yields increase with increasing bromine concentration. After fairly complete removal of the oxygen at a bromine concentration of 0.002 mole per liter and light intensity of 500 ergs per second the quantum yields are approximately as follows: triphenylmethane, 1000; diphenylmethane, 250; toluene, 50; cinnamic acid, 35 molecules per quantum.

4. The heats of bromination in the absence of oxygen are as follows: triphenylmethane, 15 kcal./mole; diphenylmethane, 12; toluene, 8; cinnamic acid, 16.

5. The larger evolution of heat in the presence of oxygen indicates that an oxidation process accompanies the inhibited photochemical reaction.

6. The oxygen inhibition is greatest for toluene and cinnamic acid and least for triphenylmethane.

7. The oxygen inhibition may be explained by a competing reaction between oxygen and the free radicals which propagate the chain.

MADISON, WISCONSIN RECEIVED JULY 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DARTMOUTH COLLEGE]

Oxygen Exchange between Water and Inorganic Oxy-anions

BY G. ALEXANDER MILLS[1]

Introduction

The importance of heavy oxygen as a means of investigating the mechanism of certain reactions was recognized soon after its discovery. From preliminary studies on the exchange of oxygen between water and certain compounds, a process which depends on chemical reactions normally occurring between water and the oxygen containing solute, certain generalities concerning the molecular structure of the solute can be drawn. These investigations also have shown that the rate of reaction is often determined by the *p*H of the solution not only because some of the reactions are subject to acid or base catalysis but also because of the dependence on *p*H of the concentration of the reacting substrate. It is important to note in this connection that the rate of attainment of elementic equilibrium, in which the numbers of ions and molecules are established, is much more rapid than for isotopic equilibrium since in that case the reaction must occur many times.

Heavy oxygen reactions have been reviewed by Rietz[2] and by Day.[3] Carboxylic acids exchange both oxygen atoms,[4] only the undissociated molecule taking part in the reaction which is acid catalyzed. The rate can be related directly to hydrolysis and esterification.[5] In contrast to the rapid hydroxyl hydrogen exchange no oxygen exchange has been found for alcohols[4a,b,e] with the exception of one tertiary alcohol, trianisylmethanol, with strong polar groups. Aldehydes and ketones[4a,e,6] undergo exchange rather readily

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(1) Present address: Catalytic Development Company, Marcus Hook, Pa.

(2) Rietz, *Z. Elektrochem.*, **45**, 101 (1939).

(3) Day, *Science Progress*, **34**, 47 (1939).

(4) (a) Cohn and Urey, This Journal, **60**, 679 (1938); (b) Roberts, *J. Chem. Phys.*, **6**, 294 (1938); (c) Roberts and Urey, This Journal, **61**, 2580 (1939); (d) Herbert and Lauder, *Trans. Faraday Soc.*, **34**, 1219 (1938); (e) Senkus and Brown, *J. Org. Chem.*, **2**, 569 (1938).

(5) Roberts and Urey, This Journal, **60**, 2391 (1938), *ibid.*, **61**, 2584 (1939); Herbert and Lauder, *Nature*, **142**, 954 (1938); Datta, Day and Ingold, *J. Chem. Soc.*, 838 (1939).

(6) Herbert and Lauder, *Trans. Faraday Soc.*, **34**, 432 (1938).

and it has been shown in the latter case that this does not proceed through enolization. As is to be expected from the foregoing, sugars exchange only the oxygen of the carbonyl group[4e,7] and proteins only the oxygen of free carboxyl groups.[8] Phenol,[4a,7] acetamide,[4d] urea[4a,e] and nitrobenzene[4b] exhibit no exchange. Gaseous oxygen exchanges with water and certain other oxygen-containing compounds only at high temperature in the presence of a catalyst.[9]

The possibility of oxygen exchange between water and sulfates,[10] phosphates,[10c,11] arsenates,[10c] nitrates,[10c,11b] chlorates,[10b,c,11b] perchlorates,[11b] carbonates,[10c,12] metasilicates,[11b] borates[11b] and chromates[11b] has been investigated. These will be considered in detail in connection with the results of this paper. In general the rate is accelerated in acid solution since then the possibility of reversible anhydride formation is increased.

In addition to the foregoing list, several other oxy-anions present interesting possibilities and some of these have been studied under various conditions of temperature and *p*H. The method of density measurement which was employed does not permit a particularly exact determination of isotopic composition. The rate of reaction was therefore determined approximately by finding the time necessary for partial exchange. In general a series of experiments was made so that conclusions do not depend on a single measurement. Special attention was given to the *p*H of the solution in its effect on rate. The oxygen exchange is then related to the possible reactions of the ions present.

Experimental

Water having an O^{18} atom fraction of 86×10^{-5}, ordinary being taken as 200×10^{-5}, was obtained through the courtesy of Professor H. C. Urey. This had been prepared by fractional distillation.[13] Density measurements of water are often expressed in γ's, parts per million of excess density. One p. p. m. corresponds very nearly to an O^{18} atom fraction of 1×10^{-5} (220 p. p. m. = O^{18} atom fraction of 200×10^{-5}).

A weighed amount of the inorganic salt was dissolved in a definite amount of this water and the solution kept at a constant temperature. After a certain time the water was distilled off *in vacuo*, purified and analyzed for O^{18}. The amount of exchange was then determined by comparison with the theoretical O^{18} value for complete reaction calculated from the weights of salt and water and their original O^{18} contents.

The O^{18} concentration of the water was determined by measuring the rate of fall of a drop of water of uniform size through an immiscible liquid of slightly lower density. This method of determining the density of liquids[14] has been adapted to the determination of deuterium.[15] It has the advantages of being rapid, requiring small volumes of liquid and having fairly high precision. The type of micropipet employed was similar to that described by Keston, Rittenberg and Schoenheimer. A screw turned through a fixed angle moves a plunger, operating through a vacuum tight rubber disk, into a capillary filled with mercury which, in turn, forces out a drop of water of uniform volume. By constructing the tip higher than the plunger much of the difficulty in maintaining an air-tight system was avoided. For water containing less than the natural abundance of O^{18} *m*-fluorotoluene possesses the most suitable coefficient of expansion for the medium liquid. The best temperature was found to be 19.33° and temperature variations were about ±0.002°. Under these conditions in order to fall 15 cm. a 9 cmm. drop of ordinary water requires about ninety-five seconds and of the "light oxygen water" about one hundred and thirty seconds. The average deviation of six readings was usually 1.5 seconds or less corresponding to an O^{18} atom fraction precision of 4×10^{-5}. The total change of O^{18} atom fractions was usually about 50×10^{-5}. The velocity of fall is a linear function of the difference in density between drop and medium within the limits used here. For a drop falling according to Stoke's law, A is a function of temperature and drop

$$\text{Oxygen}^{18}\text{ atom fraction} = \frac{A}{\text{time}} + B$$

size and B depends on temperature. A and B were evaluated by substituting the times of fall of ordinary water and of water whose O^{18} atom fraction was known to be 86×10^{-5} from analysis using a mass spectrograph.

Purification of the water from the inorganic compounds was relatively simple and usually consisted of repeated distillations *in vacuo*. However, it was sometimes necessary to add small amounts of chromium trioxide and alkaline permanganate. The apparatus used is shown in Fig. 1. The ease of removal of the central piece for cleaning is of great convenience. One-half cc. of water is ample to make two separate analyses of six readings each and to flush out the pipet.

The deuterium content of the light oxygen water may be expected to have decreased during its preparation by distillation and at a rate faster than for the O^{18}.[16] However, the effect of this diminution cannot be very great since the

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[7] Kaozumi and Titani, *Bull. Chem. Soc. Japan*, **13**, 463 and 607 (1938).

[8] Mears, *J. Chem. Phys.*, **6**, 295 (1938); Mears and Sobotka, THIS JOURNAL, **61**, 880 (1939).

[9] Morita and Titani, *Bull. Chem. Soc. Japan*, **12**, 104 (1937); **13**, 357, 601 and 656 (1938); **14**, 9 (1939).

[10] (a) Datta, Day and Ingold, *J. Chem. Soc.*, 1968 (1937); (b) Titani and Morita, *Bull. Chem. Soc. Japan*, **13**, 667 (1938); (c) Titani and Goto, *ibid.*, **14**, 77 (1939).

[11] (a) Blumenthal and Herbert, *Trans. Faraday Soc.*, **33**, 849 (1937); (b) Winter, Carlton and Briscoe, *J. Chem. Soc.*, 131 (1940).

[12] (a) Mills and Urey, THIS JOURNAL, **61**, 534 (1939), *ibid.*, **62**, 1019 (1940); (b) Titani, Morita and Goto, *Bull. Chem. Soc. Japan*, **13**, 329 (1938).

[13] Huffman and Urey, *Ind. Eng. Chem.*, **29**, 531 (1937).

[14] Barbour and Hamilton, *Am. J. Physiol.*, **69**, 654 (1924).

[15] Vogt and Hamilton, *ibid.*, **113**, 135 (1935); Keston, Rittenberg and Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937).

[16] Urey, Pegram and Huffman, *J. Chem. Phys.*, **4**, 623 (1936).

total concentration of deuterium corresponds to a density of only 16 p. p. m.[17] Hydrogen, purified by passage through acid permanganate, concentrated sulfuric acid, a saturated solution of sodium hydroxide, copper at 400° and over phosphorus pentoxide, was bubbled into a sample of the original light oxygen water in contact with platinum black for one hundred hours. Two other samples of water were carefully prepared by electrolyzing some of the original light oxygen water, made alkaline with sodium hydroxide, in an all glass apparatus using nickel electrodes and recombining the oxygen obtained with purified hydrogen over copper at 400°. These three samples were carefully compared to the original water and no density difference observed within experimental error, 4 p. p. m. Of course tank hydrogen may be expected to have a diminished deuterium content corresponding to perhaps 5 p. p. m. due to its preparation by electrolysis. In calculating the O^{18} concentration from density measurements no correction for deuterium was made. The use of light rather than heavy oxygen water has thus the distinct advantage of avoiding the rather large corrections for altered deuterium concentration.

The results of the experiments are given in Table I. When sodium hydroxide was present it was formed by addition of sodium metal to the water before introduction of the salt. Column 6, O^{18} calculated, refers to the O^{18} atom fraction calculated on the basis that all the oxygen in the water and salt have arrived at equilibrium. In a few cases, indicated by parentheses, not quite all the salt dissolved though calculations were based on all the salt present. In column 7, O^{18} observed, the results of the analysis of the water removed from the solution are given. Column 8, Exchange, indicates how far the reaction has proceeded. For cases of complete reaction there is seen to be good agreement between O^{18} calculated and O^{18} observed.

Discussion of Results

Pyrex Glass.—Experiment 1 shows the effect of the reaction between Pyrex glass and a strongly alkaline solution at high temperature. No exchange was observed even though the glass was markedly etched.

Sulfate.—Datta, Day and Ingold[10a] reported that neutral sulfates do not exchange in twenty-four hours at 100° but that the reaction is strongly catalyzed by hydroxyl ion. Titani and Goto[10b,c] confirmed the first observation and found that potassium hydrogen sulfate undergoes exchange. Winter, Carlton and Briscoe,[11b] however, do not observe exchange under any of the above conditions. They suggest that, in view of the rapid exchange of sodium metasilicate, the reaction between glass and the strongly alkaline solution may account for the observed exchange in such cases. As previously mentioned, however, only very small exchange with Pyrex glass occurs. Perhaps different glasses react differently. Experiments 10 and 11 indicate the partial exchange of potassium hydrogen sulfate. Experiment 12 shows that water held by this hygroscopic salt was not responsible for the observed result. In view of the critical dependence of rate on *p*H as shown in detail for the bicarbonate ion[12a] it is possible that the purity of the potassium hydrogen sulfate may account for the differences in observations. The bisulfate used here had an assay of 36.3% as sulfuric acid, theoretical being 36.1%. The oxygen exchange of sulfates in acid solution is in agreement with the mechanism whereby reversible anhydride formation occurs, $H_2SO_4 = H_2O + SO_3$. Acid solution favors this since then larger concentrations of acid and anhydride are present.

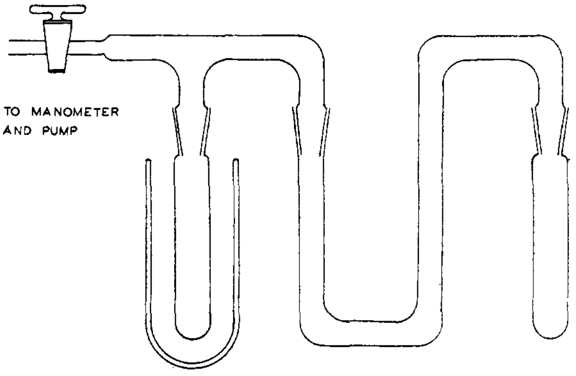

Fig. 1.

Chromate.—The oxygen exchange between water and chromates is shown by expts. 3, 5, 7 and 8. The effect of alkali is to retard greatly but not eliminate the reaction, expts. 4, 6 and 9. The partial exchange of sodium chromate at 19.3°, experiment 3, is in agreement with the recently reported[11b] value for the half-life time of four and one-half hours. The rapid exchange between water and chromium trioxide is indicated by experiment 2.

Two reactions may be suggested as possible mechanisms of exchange

$$Cr_2O_7^{--} + H_2O = 2HCrO_4^- \qquad (1)$$

$$CrO_3 + H_2O = H_2CrO_4 = H^+ + HCrO_4^- \qquad (2)$$

Reaction (1) may be written for all the isotopic oxygen varieties of the ions and molecules. Let α and β be the O^{18} atom fractions in the $HCrO_4^-$ and H_2O, respectively, and k_1 and k_{-1} be the spe-

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[17] Swartout and Dole, THIS JOURNAL, 61, 2025 (1939).

TABLE I

OXYGEN EXCHANGE BETWEEN WATER AND INORGANIC OXY-ANIONS

Original O^{18} atom fraction, of water 86 × 10^{-5}; of anions 200 × 10^{-5}; precision of analysis, ±4 × 10^{-5}

Expt.	Substance	g.	Temp., °C.	Time, hr.	O^{18} calcd.	O^{18} obsd.	Exchange
					Atom fraction × 10^{-5}		
1	NaOH	0.053	110	39	...	86	None
	H_2O (Pyrex glass)	1.024					
2	CrO_3	5.517	19.3	1.5	129	126	Complete
	H_2O	4.672					
3	Na_2CrO_4	3.589	19.3	23	(117)	99	Partial
	H_2O	4.178		96			
					(117)	110	Complete
4	Na_2CrO_4	1.021	19.3	23	(124)	86	None
	H_2O	1.998					
	NaOH	0.106		96	(124)	86	None
5	Na_2CrO_4	2.770	70	2	119	117	Complete
	H_2O	2.609					
6	Na_2CrO_4	2.763	70	2	118	106	Partial
	H_2O	2.825					
	NaOH	0.160					
7	Na_2CrO_4	2.959	110	3	129	125	Complete
	H_2O	2.272					
8	Na_2CrO_4	1.520	110	17	122	118	Complete
	H_2O	1.392					
9	Na_2CrO_4	1.184	110	3	124	117	(Nearly complete)
	H_2O	1.033					
	NaOH	0.230					
10	$KHSO_4$	1.194	100	26	126	113	Partial
	H_2O	1.216					
11	$KHSO_4$	1.722	100	24	132	126	Partial
	H_2O	1.418					
12	$KHSO_4$	1.055	100	1 min.	118	89	None
	H_2O	1.482					
13	K_2SO_3	2.257	19.3	0.5	112	88	None
	H_2O	2.677		24	112	84	None
14	K_2SO_3	0.771	100	24	112	91	None
	H_2O	.959					
15	H_2O (Na amalgam)		100	10 min.	...	86	None
16	$Na_2S_2O_5$	.788	19.3	1	113	107	Partial
	H_2O	1.247					
17	$Na_2S_2O_5$	1.914	19.3	3	115	107	Partial
	H_2O	2.810					
18	$Na_2S_2O_5$	1.586	19.3	24	116	109	Partial
	H_2O	2.234					
19	$K_2S_2O_3$	2.435	19.3	2	121	89	None
	H_2O	1.605					
20	$K_2S_2O_3$	2.540	100	24	139	133	Complete
	H_2O	0.867					
21	$K_2S_2O_3$	1.798	100	2	132	101	Partial
	H_2O	0.794					
22	$K_2S_2O_8$	3.050	100	4	129	84	None
	H_2O	1.419					
	NaOH	0.113					
23	$KMnO_4$, H_2O	Twice satd.	100	1	(134)	104	Partial
24	$KMnO_4$	a 1.983, b 1.613	100	24	(141)	131	Complete
	H_2O	a 2.051, b 1.743					

Materials: C. P. Baker Analyzed chemicals were used with the exception of the potassium thiosulfate. Sodium chromate was prepared by heating $Na_2CrO_4{\cdot}10H_2O$ for two hours at 110°. CrO_3, assay 99.8%, was used directly. Potassium hydrogen sulfate, assay 36.3% as sulfuric acid (theoretical 36.1%), was ground fine and heated at 100° for two hours. Potassium sulfite was dried at 100° for one hour. $Na_2S_2O_5$, assay 66.1% as sulfur dioxide (theoretical 67.4%), was used directly. C. P. potassium thiosulfate was ground fine and heated for two hours at 100°. It dissolved in water to form a clear solution faintly basic to litmus.

cific rate constants for the forward and backward reactions. Then, substituting in the concentrations of these ions and molecules expected if statistical distribution of the isotopes exists, for example $(HCrO^{16}O^{16}O^{18}O^{18-}) = 6(1 - \alpha)^2\alpha^2 (HCrO_4^-)$, the rate of decrease of the O^{18} concentration of the water is given by

$$-(H_2O)\frac{d\beta}{dt} = k_1\,(H_2O)(Cr_2O_7^{--})\beta - k_{-1}(HCrO_4^-)^2\alpha$$

Since elementic equilibrium exists

$$k_1(H_2O)(Cr_2O_7^{--}) = k_{-1}(HCrO_4^-)^2$$

and so

$$-(H_2O)\frac{d\beta}{dt} = k_1\,(H_2O)(Cr_2O_7^{--})(\beta - \alpha)$$

Let M and N be the total amounts of oxygen in the water and chromate ions, respectively. Therefore

$$\beta_\infty{\cdot}M + \beta_\infty{\cdot}N = \beta{\cdot}M + \alpha{\cdot}N$$

where $\beta\infty$ is the equilibrium atom fraction of O^{18}, and so

$$\frac{-d\beta}{dt} = k_1(Cr_2O_7^{--})\left(1 + \frac{M}{N}\right)(\beta - \beta_\infty)$$

and

$$t_{1/2} = \frac{0.69}{k_1(Cr_2O_7^{--})\left(1 + \frac{M}{N}\right)} \qquad (3)$$

$k_1(H_2O)$ has been measured[18] and equals 529 min.$^{-1}$ or k_1 equals 9.6 min.$^{-1}$. For a 4 molal sodium chromate solution, $M/N \approx 3$, the concentration of $Cr_2O_7^{--}$ is calculated to be 3×10^{-6} from the equilibria[19]

$$\frac{(HCrO_4^-)^2}{(Cr_2O_7^{--})} = 0.02 \quad\text{and}\quad \frac{(H^+)(CrO_4^{--})}{HCrO_4^-} = 6 \times 10^{-7}$$

Substitution of these values yields $t_{1/2} = 10^4$ minutes as compared to the experimental value of 260. It therefore appears that reaction (1) is not rapid enough to account for the exchange and that reaction (2) is probably the mechanism. No inference can be drawn from the rapid exchange of CrO_3 since in that case both reactions would result in very rapid exchange.

Sulfite.—No exchange was observed for potassium sulfite after twenty-four hours at 100°.

Sodium metabisulfite undergoes some exchange under the conditions of expts. 16, 17 and 18. In order to distill off the water it was necessary to add sodium amalgam to the cold solution, followed by redistillation from small amounts of chromium trioxide. Experiment 15 shows that these reagents result in no alteration to the O^{18} concentration. The results are not wholly satisfactory since as the time is increased the fraction of exchange does not increase proportionately. It is to be expected that in these bisulfite solutions more exchange would take place than in the sulfite solutions due to the greater concentration of sulfur dioxide.

Thiosulfate.—At 100° potassium thiosulfate exchanges as shown by expts. 19, 20 and 21. In the latter case the reaction is only partially complete. Experiment 22 shows that in alkaline solution the rate is so decreased that no exchange can be detected. Thiosulfuric acid is a strong acid and the thiosulfate ion might be expected to behave like the sulfate ion and exhibit no exchange. The instability of the $HS_2O_3^-$ ion may account for this difference.

Permanganate.—Since potassium permanganate is not very soluble the experiments were done in two steps, the water obtained from the first part being used with a new sample of salt. Several hours are required at 100° for complete reaction. The exchange may proceed through permanganic acid or it may occur due to reactions which may be represented by

$$2KMnO_4 + MnO_2 + 4KOH = 3K_2MnO_4 + 2H_2O$$

Mechanism of Exchange.—Oxygen exchange between water and inorganic oxy-anions may be supposed to take place in three general ways: (a) direct interchange of oxygen atoms; (b) addition and subsequent removal of H_2O or OH^- to the anion with possibility of exchange; (c) hydrolysis to form undissociated acid followed by reversible anhydride formation. There has been no evidence that mechanism (a) occurs. In general all exchange can be ascribed to chemical reactions normally occurring between water and solute. For certain anions mechanism (b) is possible. In the case of the chromate ion the corresponding reaction has been shown to be too slow

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[18] LaMer and Read, THIS JOURNAL, **52**, 3098 (1930).

[19] Saal, *Rec. Trav. Chim.*, **47**, 264 (1928); Sherrill, THIS JOURNAL, **29**, 1641 (1907).

to account for the observed rate. Mechanism (c) has been demonstrated to account quantitatively for the observed rate for bicarbonate ion.[12a] The salts which do experience exchange are usually those derived from a weak acid. When exchange is due to reversible anhydride formation, the rate will depend on the rate of the chemical reactions, which are usually rapid, and on the concentrations of the substances which actually take part in the reaction, that is, the amounts of undissociated acid formed by hydrolysis and also the fraction of this in the form of anhydride. The rate depends very critically on these widely variable quantities as can be seen from the calculations given in connection with the chromate ion. In agreement with the expected exchange of salts of weak acids due to greater hydrolysis, sodium metasilicate, borax, sodium carbonate and sodium chromate are known to exchange rather readily. On the other hand, potassium chlorate, potassium perchlorate and potassium sulfate, salts of strong acids, do not undergo exchange under similar conditions. However, in acid solution exchange then occurs due to the shift of equilibrium to form the anhydride. The fact that potassium permanganate and potassium thiosulfate, salts of strong acids, exhibit exchange may be due to relatively large amounts of anhydride present or reactions other than anhydride formation.

Summary

Oxygen exchange between water and Pyrex glass, sodium chromate, potassium hydrogen sulfate, potassium sulfite, sodium metabisulfite, potassium thiosulfate, and potassium permanganate has been studied under conditions of varying temperature and pH. The results are discussed in terms of the chemistry of these compounds.

The oxygen exchange between water and sodium chromate is shown to proceed at a rate faster than can be accounted for by the reaction

$$Cr_2O_7^{--} + H_2O = 2HCrO_4^-$$

The rate of oxygen exchange of inorganic oxyanions is related to the acid strength of the corresponding acid. The mechanism of hydrolysis followed by reversible anhydride formation is shown to account for the observed exchange reactions.

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Determination of the Surface of Powders

BY FRANK B. KENRICK

Several principles have been employed in the past as a basis for estimating the surface area of irregular solid particles. The following principle is, I believe, new.

It can be shown easily that the average of the areas of the projections of a unit plane area of any shape in all random positions is one-half. The surface of any solid figure in all random positions may be considered as made up of a number of plane surface elements in all random positions, and the sum of the averages of the projection areas of these will therefore be one-half the total area of the figure. In whatever position the figure may be, provided there are no re-entrant angles, exactly half the projection areas of these elements will be masked by the other half, and consequently the average projection area of any such figure in all random positions is one quarter of the total area of the figure. For example, the average projection areas of a sphere of radius 1, a cube of side-length 1, and a plate $1 \times 1 \times 0$ are π, 1.5, and 0.5, respectively. Their actual areas are 4π, 6 and 2.

The average projection areas of a large number of particles in random positions may be determined from planimeter measurements of outlines made on a screen image of a microphotograph of the particles, and this value will approach the average projection areas of particles in all random positions as the number of particles increases. By multiplying this value by four and by the number of particles the true area is given, except for re-entrant angles, and except for any fine-grained roughness which escapes observation in the images. Careful examination of a large number of particles showed that, apart from slight undulations, re-entrant angles were of infrequent occurrence, and examination of a number of large fracture surfaces of glass indicated that the occasional sets of sharp striations formed only a small fraction of the total surface.

Several methods of obtaining random positions of the particles on a slide are described by Mr. Birnie in the next article, "Adsorption of Water Vapor on Silica"; the close agreement of the values obtained by the several methods shows that the methods are satisfactory.

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