

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

The Densities of Fine Powders

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No little work has been done in recent years on the problem of the densities of fine powders and especially those powders having a porous structure. Cude and Hulett¹ found in determining the density of charcoal in carbon disulfide, water, benzene and carbon tetrachloride that the apparent density, as determined in the different liquids, decreased in the order named. From a study of their results the conclusion was reached that the density values varied due to different degrees of penetration of the porous microstructure of the powder by the different liquids, the degree of penetration being governed by the surface tension and the fluidity of the liquids. Harkins and Ewing² also working with active charcoal made density determinations in a number of liquids. A similar variability was obtained though not in entire agreement with Cude and Hulett. They concluded that a compression of the liquid film at the solid-liquid interface caused the apparent density of the powder to be abnormally high and that the liquids with the greatest compressibility gave to the powder the greatest density. Later Howard and Hulett³ with new data opposed the theory of film compression. Lamb and Coolidge⁴ studying the heats of adsorption of vapors on charcoal found that the data gave support to the theory of a compressed layer at the solid-liquid interface and M. W. Tschapek⁵ indicated that his density measurements of several solids in water and benzene lead to the same conclusion.

It appeared to the writers that a reconsideration of the apparent densities of two solids of quite different character as measured in each of a group of liquids should give a better concept of the causes of their variations in value. To this end the densities of silica gel and an active charcoal were determined in each of four different liquids.

Materials

All materials were carefully prepared or purified. The solids used were silica gel and an active

(practically ash free) charcoal. The liquids were water, benzene, carbon tetrachloride and petroleum ether. The best laboratory reagent quality of the organic liquids was selected and each of these was specially purified. The purification in each case was concluded with thorough treatment with dehydrating agents in order to ensure completely anhydrous liquids, phosphorus pentoxide being used with carbon tetrachloride and sodium with benzene and petroleum ether.

Silica gel was prepared by precipitation from sodium silicate solution with ferric chloride by the method of Holmes, Sullivan and Metcalf.⁶ After drying, the gel was pulverized in a pebble mill and screened through a 200-mesh screen.

Carbon was prepared from a commercial active charcoal, the mineral content being removed by the method of E. J. Miller.⁷ The final treatment was to heat to approximately 900° in a closed crucible for a period of two hours. Analysis of this product showed it to have an ash content of $0.02 \pm 0.005\%$.

Procedure

The density determinations were made by enclosing 2 to 3 g. samples of the solid in Pyrex bulbs and evacuating the bulbs while their temperature was maintained at $475 \pm 20^\circ$. After evacuation the bulbs were sealed off while still hot, cooled, weighed in air, and then the tip, at the point of sealing, broken off under the surface of a portion of the freshly degassed liquid. The bulb was then suspended in the liquid by means of a loop of fine platinum wire and weighed while immersed. After emptying the bulb, it was reweighed in the liquid and in air, the tip broken off when the bulb was opened being accounted for in the latter weighing. Calculation of the density may be summarized in the following formula, after Lowry⁸

$$S = \frac{A - B}{[(A - B) - (C - D)]/d}$$

where A = weight glass and sample in vacuum

B = weight glass in vacuum

C = weight glass and sample in the liquid

(1) Cude and Hulett, *THIS JOURNAL*, **43**, 391-401 (1920).

(2) Harkins and Ewing, *ibid.*, **43**, 1787-1802 (1921).

(3) Howard and Hulett, *J. Phys. Chem.*, **28**, 1082-1095 (1924).

(4) Lamb and Coolidge, *THIS JOURNAL*, **42**, 1146-1170 (1920).

(5) Tschapek, *Kolloid. Z.*, **63**, 34-6 (1933).

(6) Holmes, Sullivan and Metcalf, *Ind. Eng. Chem.*, **18**, 386 (1926).

(7) Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

(8) Lowry, *THIS JOURNAL*, **46**, 824 (1924).

D = weight glass in liquid

d = density of the liquid

The bulbs were evacuated by means of an oil pump. For the charcoal a period of eight to ten hours of evacuation was required and for the silica gel thirty-six to forty hours. Not having available a McLeod gage, the exact air pressure in the bulbs was not known, yet these periods were found to be of sufficient length that longer evacuation yielded no appreciable change in the density values. The final weighings of the sample suspended in the liquid were made approximately two hours after the sample was wetted. This procedure does not eliminate all the effect of the drift discussed by Cude and Hulett,¹ but from an inspection of the curves presented by these authors and from the reproducibility of the results found in the present investigation when weighings were made from one and one-half to two and one-half hours after wetting, it was concluded that the method adopted yielded values that might be confidently used for purposes of comparison.

Results and Discussion

The values of the densities of the active charcoal and silica gel in each of the four liquids are presented in Table I.

TABLE I
APPARENT DENSITIES OF CHARCOAL AND SILICA GEL AT 25°

	Charcoal, g./cc.	Silica gel, g./cc.
Water	1.821	2.246
Benzene	1.994	2.149
Carbon tetrachloride	1.860	2.132
Petroleum ether	2.083	2.125

It is interesting to note that in this restricted group, water, the liquid which yields the highest density for silica, yields the lowest density for charcoal, while the petroleum ether which yields the highest density for charcoal yields the lowest density for silica. It is the special purpose of this paper to point out this fact and to consider its consequences. The same sort of inverted relationship is seen between water and benzene, benzene and petroleum ether, water and carbon tetrachloride, carbon tetrachloride and petroleum ether but not between benzene and carbon tetrachloride. It should be stated immediately, however, that this inverted relationship is not as general as is indicated by the data from this group of liquids. Further work in this Laboratory⁹ with other liquids develops such a point

(9) Culbertson and Weber, unpublished data.

but the argument presented below is proposed with this fact in mind and is in no sense invalidated by it. In this series it is quite possible that the benzene-carbon tetrachloride relationship is affected by an abnormal condition of the charcoal-carbon tetrachloride system. This is suggested by the work of Pearce¹⁰ who concluded that some decomposition of the carbon tetrachloride occurred at the charcoal surface and also, for the reasons discussed below, by his observation that the heats of adsorption of the chlorine substituted methanes increased with increased chlorine content up to the tri-substituted compound, then dropped off for the tetrachloride.

It is obvious that an adequate theory of the differences in the apparent density of a solid as indicated by different liquids must harmonize with the situation presented by the above data. This point is strengthened by the fact that the results are in good agreement with the values obtained for charcoal in most of the investigations noted above and for silica in the work of Tschapek.⁵

A consideration of the theories presented by the other workers, however, in the light of the values for the two solids, reveals certain elements of inconsistency. If the liquids penetrated the microstructure of the solids to different degrees as a result of differences in molecular size, fluidity or surface tension of the liquids themselves, it would be impossible for the situation indicated by these data to obtain: *e. g.*, high density of silica in water and low density of carbon in the same liquid. It is equally true that if the compressibility of the liquids were the sole factor involved then the observed data would hardly be explicable.

It appears to the writers that the mutual relation between liquid and solid at the interface must be of vital importance. Of all the highly porous insoluble powders readily obtained, charcoal seems to be more organophilic in nature than any other. This statement very probably will have a surer foundation if we limit it to the organic compounds of non-polar type. On the other hand, the silica gel is distinctly hydrophilic. The tentative hypothesis would be offered then that the observed variations in density are due to one or the other of the following factors: first, differences in the degree of penetration of the porous solid by the liquids as a result of differences

(10) Pearce, *J. Phys. Chem.*, **34**, 1280-1279 (1930).

in the surface energy decrease on wetting; or second, differences in the degree of compression of the liquids at the solid-liquid interface as determined, primarily, by the different forces of attraction at the interfaces and, secondarily, by the different compressibilities of the liquids. The results obtained as yet are such that either or both of these factors may be of significance. In case the liquid compression is dominant it is clear that the interfacial force or energy relations are of greater importance than the actual compressibilities of the liquids, for the reason mentioned above in connection with the compression theory. Either of the above postulates requires an intimate relation between density values and the decreases in surface energy when the solid is wetted by the liquids. The complexity of the situation, however, involving the unknown specific areas of the solids used and the possible subordinate role of the compressibilities of the liquids, renders the quantitative treatment of this relation yet impossible.

A comparison of the order in which the density values fall, however, with some data on other interfacial phenomena such as adhesion tensions¹¹ and heats of wetting,¹² shows a rather striking similarity which seems to offer strong support for the postulates advanced.

Summary

Measurements of the apparent densities of charcoal and silica gel in water, carbon tetrachloride, benzene and petroleum ether have been made. The liquids, water and petroleum ether, which, respectively, show the highest and lowest apparent densities for silica yield values of the opposite order for charcoal. Some existing theories are examined in the light of the data found and a new postulate advanced.

(11) Bartell and Osterhoff, *J. Phys. Chem.*, **37**, 543 (1933).

(12) Patrick and Grimm, *THIS JOURNAL*, **43**, 2144-2150 (1921); Bartell and Almy, *J. Phys. Chem.*, **36**, 985-999 (1932); Andress and Berl, *Z. physik. Chem.*, **122**, 81-86 (1926); Culbertson and Winter, unpublished data.

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Heats of Wetting of Activated Charcoal and Silica

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The results of a recent investigation in this Laboratory¹ on the apparent densities of active charcoal and silica gel, when various liquids were used as the buoying fluids, led to the suggestion that a significant relation existed between the density values and the interfacial energy changes when the solids were wetted by the liquids. In particular it was pointed out that when the apparent density values as found by immersion in the different liquids were arranged in increasing or decreasing order, then the corresponding values of the heats of wetting of similar solids by the liquids, as recorded by a number of investigators, were found in most cases to be in the same order. Since, in the investigation referred to, a considerable quantity of both the active charcoal and silica gel had been prepared, it was considered an excellent opportunity to study the heat of wetting characteristics of the solids when samples were available which were identical in all respects with the material used in the density determinations. In making these latter determinations the samples

had been enclosed in glass bulbs and evacuated at elevated temperatures before immersion. It was decided therefore that, though in most of the studies of heats of wetting found in the literature non-evacuated samples were used, a technique must be adopted which would put the solid in approximately the same condition as it had been in the density measurements.

To accomplish this end the samples were enclosed in specially designed glass bulbs and evacuated at 220° for thirty-six hours by means of an oil pump. After sealing off the bulbs while still hot, the latter were cooled and weighed. Wetting of the sample in the calorimeter was accomplished by crushing the bulb, a mechanism being employed which permitted this to be accomplished without opening the calorimeter. This mechanism consisted of a steel holder so arranged that a screw, projecting through the calorimeter closure and operated by hand, compressed the bulb supports. A one-liter Dewar cylindrical flask closed with a thick tightly fitting cork served as the calorimeter. This was set in a water-bath main-

(1) Culbertson and Dunbar, *THIS JOURNAL*, **59**, 306 (1937).