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 tensions[11] 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 Chem.*, **122**, 81–86 (1926); Culbertson and Winter, unpublished data.

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

Heats of Wetting of Activated Charcoal and Silica

BY J. L. CULBERTSON AND L. L. WINTER

The results of a recent investigation in this Laboratory[1] 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-

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

tained at 25 ± 0.1°. A motor-driven stirrer operated in the calorimeter throughout a determination and the heat capacity of the entire assembly was determined immediately after each run. This was accomplished by means of a measured amount of electrical energy introduced through a resistance wire. Temperature differences were read from a Beckmann thermometer.

Materials.—In the previous investigation referred to, four liquids had been used in determining the densities of the solids. These were water, benzene, carbon tetrachloride and petroleum ether. For the present work these were used and were prepared in the same way as in the previous study. In addition, two other liquids were prepared and used, nitrobenzene and carbon disulfide. The nitrobenzene was treated with sodium hydroxide, washed with water, and dried with calcium chloride. It was then distilled three times, a constant boiling middle portion being secured. The carbon disulfide was treated with mercury and with mercuric chloride, washed with water and dried with phosphorus pentoxide. It was then distilled three times as was the nitrobenzene. The solids, charcoal and silica gel, were portions of the same materials as were used in the density determinations and their preparation has been described in the report of that work.

Results and Discussion.—The values obtained for the heats of wetting of the two solids by the various liquids are indicated in Table I. Three values for each case show the order of agreement in duplicate determinations.

In general it may be said that the heats of wetting of silica gel agree well with those found by Berthon,[2] Patrick and Grimm,[3] and Bartell and Fu,[4] though somewhat greater differences between the values for the organic liquids are observed. With the charcoal the agreement with other workers is not so close due no doubt to the wide variations in charcoal used by different investigators. It is believed by the writers that these data represent very reliable values for the systems named because of the care used in evacuating the samples and also because of the fact that in the case of the charcoal, virtually ash free samples were used. The latter point seems especially significant for in view of the relationship between the heats of wetting of the water and the organic liquids on silica it appears that even a moderate percentage of mineral content in the charcoal would alter entirely the heat of wetting relationship. This is well substantiated by a glance at the tables of the "I. C. T."

TABLE I

HEATS OF WETTING OF SILICA AND CHARCOAL

Liquid	$-\Delta H$ on silica, cal./g.	$-\Delta H$ on charcoal, cal./g.
Water	16.0	8.5
	16.2	8.5
	15.9	8.3
Average	16.0	8.4
Nitrobenzene	14.3	27.1
	14.5	27.2
	14.2	27.0
Average	14.3	27.1
Benzene	10.9	20.8
	11.4	21.2
	11.2	21.2
Average	11.2	21.0
Carbon disulfide	6.5	29.2
	6.7	29.6
	6.8	29.6
Average	6.7	29.5
Carbon tetrachloride	6.1	19.7
	6.3	20.1
	6.5	20.2
Average	6.3	20.0
Petroleum ether	4.1	23.7
	4.3	23.9
	4.5	23.8
Average	4.3	23.8

Of especial interest is the fact that water with the highest heat of wetting on silica yields the lowest value on charcoal. It is also noteworthy that the petroleum ether, exhibiting the lowest heat change with silica, shows a high, though not the highest in the group, heat of wetting on charcoal. Qualitatively these relationships show clearly that the two fundamentally different types of solids, silica and charcoal, possess quite different energy change characteristics when wetted by liquids. In broad terms this is summed up in the statement that the charcoal undergoes a high energy change at the solid–liquid interface when wetted by organic liquids and relatively low change when wetted by water. The exactly opposite situation is obtained in the case of the silica gel. In more detail, however, it is to be noted that nitrobenzene appears in second place in each column. This probably may be interpreted to mean that on silica the polar nitro group is oriented to the solid surface while on the

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(2) Berthon, *Compt. rend.*, **195**, 1019–1021 (1932).

(3) Patrick and Grimm, THIS JOURNAL, **43**, 2144–2150 (1921).

(4) Bartell and Fu, "Colloid Symposium Annual," **7**, 135–149 (1929).

carbon the orientation is in the opposite direction, though why the latter should show such an increased heat of wetting over that of benzene is not obvious.

In the previous work on the densities of these solids a correlation with existing data on heats of wetting is mentioned. How well this is borne out in the present work is indicated in Table II.

TABLE II

DENSITIES AND HEATS OF WETTING OF SILICA GEL AND CHARCOAL

	Silica		Charcoal	
Liquid	Heat of wetting, cal./g.	Density, g./cc.	Heat of wetting, cal./g.	Density, g./cc.
Water	16	2.25[a]	8.4	1.82
Nitrobenzene	14.3	2.23	27.1	2.00[a]
Benzene	11.2	2.15	21.0	1.99
Carbon disulfide	6.7	2.21[a]	29.5	2.02[a]
Carbon tetrachloride	6.3	2.13	20.0	1.86
Petroleum ether	4.3	2.12	23.8	2.08

[a] The values so indicated are due to Culbertson and Weber (unpublished data). Identical silica gel and charcoal were used but the method of Tschapek [*Kolloid. Z.*, **63**, 34–36 (1933)] was employed in making the determinations. This method was compared with that used by Culbertson and Dunbar and satisfactory checks were obtained.

For the most part high heats of wetting accompany high densities though carbon disulfide on silica appears to provide an exception to such a generalization. It is the contention of the writers, however, that such evidence as these data afford tends to confirm the ideas expressed in the paper by Culbertson and Dunbar,[1] *e. g.*, that differences in the apparent density of a porous solid as indicated by measurements made with different liquids as filling fluids are due either to differences of penetration of the pores of the solid by the liquids or to differences in the amount of compression of the liquid film at the interface, in either case the determining factor being the decrease in surface energy when the liquid wets the solid. Quantitative correlation is of course lacking in Table II, but in consideration of the fact that if the above view of these phenomena is correct, then the specific areas of the solids, the compressibilities and the heats of compression of the different liquids, satisfactory data for most of which are unavailable, would have to be taken into consideration in developing such quantitative ideas and therefore the irregularities found are quite within the expected magnitude.

Summary

The heats of wetting of charcoal and silica gel by water, nitrobenzene, benzene, carbon tetrachloride, carbon disulfide and petroleum ether have been determined. A correlation is noted between the order in which these values fall and that of the apparent densities of the solids as determined in the same liquids.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Accumulation of Alkali Promoters on Surfaces of Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND S. BRUNAUER

It has been pointed out repeatedly that the high pressure activity of iron synthetic ammonia catalysts containing a per cent. or so of potassium oxide in addition to an approximately similar amount of aluminum oxide is considerably greater than that of a catalyst promoted with aluminum oxide alone.[1] So far as we are aware, however, no evidence has ever been published concerning the fraction of the catalyst surface actually covered by the few per cent. of the alkali oxide promoters contained in typical iron synthetic ammonia catalysts. It is the purpose of the present paper to show that some recently determined low temperature adsorption isotherms of nitrogen, carbon monoxide and carbon dioxide on five different synthetic ammonia catalysts, enable us to conclude that 1% or so of potassium oxide in a catalyst actually covers a large fraction of the catalyst surface.

Experimental

The adsorption apparatus used was similar to that already described[2] except that parts F, E, C′, C, M, A, N, L, K, J and trap H of the apparatus shown in Fig. 1 of that paper were eliminated, and a manometer made of 10-mm. tubing was attached at the top of buret B. Stopcocks 1 and 2 were replaced by mercury sealed vacuum cocks, and catalyst bulb A was replaced by one of 25-cc. capacity.

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(1) Larson, *J. Ind. Eng. Chem.*, **16**, 1002 (1924); Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

(2) Emmett and Brunauer, THIS JOURNAL, **56**, 35 (1934).