The deviation of the values of individual rate constants from the mean is appreciably greater than is usually found where a single mixture can be followed with time, yet no correlation between the deviations and the concentrations of reactants or products is evident.

It must be pointed out that iodine monochloride dissociates[1] somewhat (3% at 210°) into iodine and chlorine, and that a mechanism involving the possible reaction of hydrogen with chlorine must be considered. Inasmuch as the dissociation is greatly repressed as soon as some free iodine is formed, and since mixtures initially containing excess iodine gave sensibly the same results, such a mechanism does not seem likely. The direct reaction between hydrogen and iodine is very slow at 240° and below.[2]

When the average values of the specific reaction rate constants are plotted against $1/T$ a straight line results. The energy of activation for the assumed slow reaction is 33,900 cal.

[1] McMorris and Yost, THIS JOURNAL, **54**, 2247 (1932).

[2] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

CONTRIBUTION FROM
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 484
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Specific Heat and Binding Conditions of Adsorbed Argon on Charcoal

BY HANS M. CASSEL

When a monoatomic gas is adsorbed at the surface of an elementary solid, the first adsorption layer represents a more or less perfect continuation of the crystal lattice. Accordingly, the "adatoms"[1] behave as being bound by certain centers of attraction around which they move similarly as the atoms of the adsorbent. But, due to the anisotropy of the situation, the oscillation perpendicular to the surface freezes in, if the temperature is enough decreased, whereas the degrees of freedom parallel to the surface, corresponding to weaker binding forces, remain still excited at much lower temperatures.

It depends on the size and shape of the potential box in which the adatom may be regarded as contained,[2] whether the movement is a two-dimensional translation or a two-dimensional harmonic oscillation. Accordingly, the specific heat of the adatoms, in the first case, has the value, R, remaining constant except at extremely low temperatures, and, in the second case, the value, $2R$, decreasing with decreasing temperature in analogy to the Debye function of the three-dimensional oscillator.

F. Simon and R. C. Swain[3] recently having measured the heat capacity of argon adsorbed on charcoal observed the rather constant value, R, between 80 and 60°K., but, at lower temperatures, a decrease leading to an almost imperceptible amount below 20°K. Thus, the experimental result agrees neither with the first nor with the second possibility explained above. Instead, the appearance of the sloping-down perfectly resembles the Debye function of a one-dimensional oscillator.

This view, indeed, is justified, since it is much more probable that an argon atom is adsorbed in the hollow edges or steps of the very cleavable material than on the smooth surfaces of the netplanes. Adatoms bound by two vicinal crystal planes, at low temperatures, are capable of only one-dimensional vibrations parallel to both surfaces. The specific heat measurements, therefore, back the suggestion that the majority of the argon atoms is adsorbed in this way.

[1] I. Langmuir, *J. Chem. Physics*, **1**, 3 (1933).

[2] The author is very much indebted to Dr. L. Pauling, Cal. Tech., for the calculation of the degeneracy temperature.

[3] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

STANFORD UNIVERSITY
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Areametric Analysis. A Useful Technique in Estimating Small Amounts of Heavy Precipitates

BY V. R. DAMERELL AND M. AXELROD

In attempting to measure small amounts (0.01 to 5 mg.) of lead sulfate in contact with sulfuric acid, the authors were able to develop a simple technique whereby compact circular (or square) piles of precipitate could be obtained, of reproducible dimensions, in the center of the flask bottom (see Fig. 1). The apparent areas of these "spots" (as viewed from above, and assuming them to be flat circles or squares) could be readily measured and compared to the areas produced by known amounts of precipitate. This method of analysis is new, according to the authors' best knowledge, and since it involves the measurement of an area, the term areametric analysis is proposed.

The method is generally applicable to heavy precipitates of the lead sulfate type, such as barium sulfate, lead arsenate, lead chromate, etc. The determination is made right in the precipitation beaker or flask, and the procedure is of such simplicity that the authors feel the method may be of considerable use in the estimation of small amounts of many substances.

The technique used in the formation of these "spots" was as follows. The liquid in the flask was first swirled twenty or thirty times, to loosen the precipitate and cause part of it to go to the center. Then after allowing the precipitate to settle for a minute or two, the flask was tipped so that the line made by the edge of the liquid crept nearly to the center of the flask bottom. Sufficient liquid was present in the flask so that the flask bottom made a maximum angle of about 60° with the desk top. This was done ten times to the left, ten times to the right, and ten times each backward and forward. The precipitate was brought to the center of the flask bottom by this procedure.

Finally the flask was held by the thumb and finger of the right hand near the bottom and the thumb and finger of the left hand near the top, over a black surface. The right hand now made a series of short backward and forward movements (about ten to a series, at the rate of three or four a second). During these movements the flask did not move more than a millimeter or two, and the force was applied by the whole forearm, the wrist being held practically stiff. After each series of shakes the flask was rotated 30 or 40°. These vibrational movements caused the precipitate to be swept into a compact circular pile. Photographs of spots obtained are given in Fig. 1.

0.01 Mg. 0.12 Mg. 0.17 Mg. 0.27 Mg. 0.63 Mg

Fig. 1.—Lead sulfate "spots."

After a few minutes of such shaking the spot reached an essentially constant, minimum size. The flask was then placed on the "standard spot" card (Fig. 2) and moved along until a spot was reached which matched the unknown spot in size. This card was simply a reduced copy of a contact photograph of a twist drill and steel wire gage. It was calibrated with known amounts of precipitate. A sheet of millimeter graph paper can be substituted for occasional determinations. This vibration method was used to obtain circles having an apparent area up to about twenty square millimeters. For larger amounts than this the minimum area of the square was obtained by the tipping process described above. The dimensions of the square could be rapidly obtained by placing the flask on millimeter graph paper.

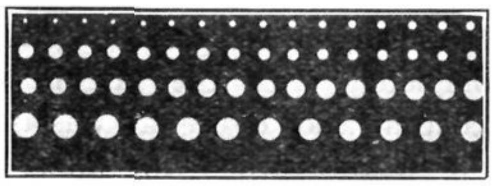

Fig. 2.

Quantitative results are given in Table I for lead sulfate in contact with 10 cc. of 40% sulfuric acid, measured in a 50-cc. Pyrex Erlenmeyer flask.

TABLE I

Mg. lead present	Mg. lead found	Impurities present, mg.	Mg. lead present	Mg. lead found	Impurities present, mg.
0.08	0.08	None	0.06	0.08	Sn (10)
.20	.19	None	.10	.13[a]	As (10) Bi (1)
.13	.14	None	.20	.19[a]	Cu (10) Cd (1)
.10	.09	None	.30	.32[a]	As (1) Bi (1) Cu (1)
.04	.06	None			Sb (1) Sn (1)
.02	.03	None	.40	.37[a]	Cu (1) Cd (1)
.04	.05	None	.50	.54[a]	Cu (10) Cd (10)
.20	.15	Cd (10)	1.0	1.3[a]	As (10) Bi (10)
.12	.10	Cu (50)			Cu (10)
.09	.10	Bi (10)	2.0	1.8[a]	Cu (5) Cd (5)
.08	.08	Bi (50)	3.0	2.7[a]	As (5) Sb (10)
.06	.12	As (50)			Sn (10)
.17	.18	Sb (10)	4.0	4.2[a]	Cu (4) Cd (4)

[a] Precipitate washed three times, redissolved and reprecipitated.

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The Catalytic Oxidation of Carbon

BY JESSE E. DAY,[1] RICHARD F. ROBEY AND HYP J. DAUBEN

A few years ago, Taylor[2] reported a means of demonstrating the peculiar catalytic effect of sodium chloride on the oxidation of soot carbon, a phenomenon well known to the layman in its practical application.

We have successfully performed the demonstration of Taylor many times; it was discovered, however, that not only sodium chloride is effec-

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(1) Because of the untimely death of Professor Jesse E. Day, on April 19, 1935, the junior authors have been deprived of the benefits of his kindly guidance and criticism in the preparation of this paper.—R. F. R. and H. J. D.

(2) R. K. Taylor, THIS JOURNAL, **52**, 3025 (1930).