The experimental results of the foregoing investigation have yielded the atomic weights of different varieties of lead as follows:

| | Atomic weight |
|---|---|
| Common | 207.21 |
| Bedford cyrtolite | 205.94 |
| Katanga pitchblende | 206.00 |
| Katanga pitchblende extract | 205.97 |

CAMBRIDGE, MASSACHUSETTS

RECEIVED APRIL 11, 1933
PUBLISHED JULY 6, 1933

# Notes

## The Specific Heat of Sorbed Matter

BY J. L. PORTER AND R. C. SWAIN[1]

The heat capacity of a substance varies considerably with the state. A study of the heat capacity of matter in the sorbed state should give some indication of the state of the sorbed molecules, whether they can move freely, vibrate, rotate, or show still more restricted motion, and also the strength or type of binding of the sorbed molecules to the solid. When the molecule is sorbed, certain degrees of freedom may be "frozen out" or suppressed.

The specific heat of bound water in crystalline hydrates is found to be about the same, in a number of hydrated salts, as that of ice, which is about half that of liquid water. The partial molal heat capacity of water in 25 mole per cent. hydrochloric acid solution is about two-thirds that of pure liquid water,[2] presumably because the permanent dipole of the water molecule is oriented and also attracted to the ion. Bridgman[3] found that at 0° and under an external pressure of 4000 kg./sq. cm. $C_p$ of water is 0.92 calories and at 0° and 6000 kg./sq. cm. pressure $C_v$ of water is 0.85 calories.

In connection with his studies on the sorption of water by charcoal, one of us (J. L. P.) prepared a system consisting of 6 g. of water sorbed in 18 g. of highly active sugar charcoal. Dr. S. B. Thomas then undertook measurements of the heat capacity of this system and, while the investigation encountered unforeseen difficulties, he was able to obtain a value of about 8.5 ($\pm$0.1) calories for this system in the neighborhood of 10°. If we then assume that the charcoal in this system has the same heat capacity per gram as graphite, we have left about 5.6 ($\pm$0.2) calories as the heat capacity of the 6 g. of sorbed water. Hence the water in this system seems to be essentially in the state of the ordinary liquid rather than in that of

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[1] National Research Fellow in Chemistry.

[2] By the graphical method of Lewis and Randall on the data in the "International Critical Tables," 1929, Vol. V, p. 85.

[3] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 359 (1912).

water in the form of ice or water of crystallization. This is quite in accordance with the observations made in this Laboratory on the sorption of water on charcoal in which the sorption of water is interpreted as the condensation of a two-dimensional liquid film on the surface of the charcoal.[4]

In order to have the specific heats of a sorbed gas in a more typical case, utilization is made of some data obtained by one of us (R. C. S.) who measured, in the laboratory of Professor F. Simon in Berlin, the specific heats of argon and hydrogen sorbed in charcoal impregnated with zinc chloride.

Exact measurements of the partial molal heat capacities at room temperatures of gases adsorbed on charcoal are very difficult because of the small number of bound gas molecules in comparison with those of the charcoal. At low temperatures, however, the specific heat of charcoal is extremely small ($C_p$ 0.25 cal./degree at 50°K.), while the specific heats of the sorbed gases remain comparatively large.

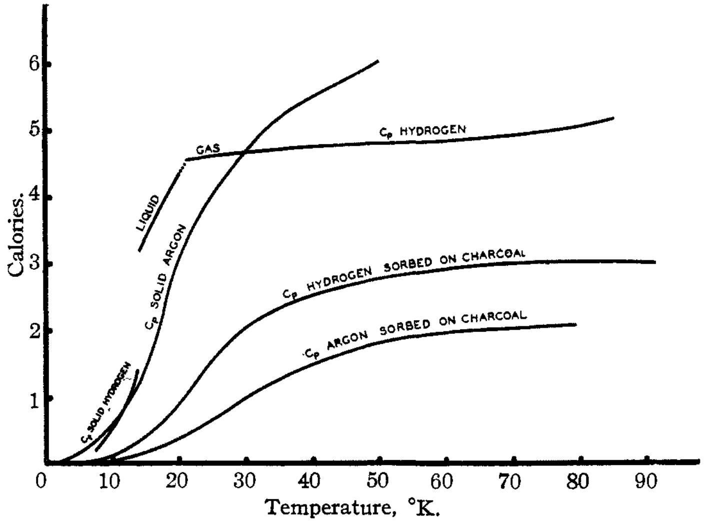

Fig. 1.—Heat capacity of argon and hydrogen in the free and sorbed state.

As is shown in Fig. 1, the heat capacity of sorbed argon is only a fraction of that of argon in the free solid state. The effect of this obviously physical adsorption is, therefore, quite as great as is that of chemical combination. Possible ways of interpreting this low value of approximately 2 cal./degree from 60–80°K. are discussed in another paper.[5]

In the case of hydrogen adsorbed on charcoal the heat capacity is also

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(4) McBain, Porter and Sessions, THIS JOURNAL, **55**, 2294 (1933).

(5) R. C. Swain, communicated to the *Z. physik. Chem.*

much below that of the free gas. However, the curve, as shown in Fig. 1, has direct quantitative significance only below 20°K. It is well known that charcoal catalytically hastens the conversion into the equilibrium mixture of ortho and para hydrogen. The amount of heat required to maintain this equilibrium mixture varies with the temperature but reaches a maximum of nearly 4 cal./mole at 40°K. Below 20°K. this effect is not noticeable, and the heat capacity of the sorbed gas is less than 20% of that of the free solid hydrogen, which seems to indicate that the sorbed molecules are held even more firmly than those in the solid state.

Finally, the low specific heat of the sorbed gases, argon and hydrogen, and the high specific heat of sorbed water is hardly to be explained by the classical hypothesis in which the sorbed substance is supposed to be under a high pressure depending only upon the coefficient *a* of van der Waals' equation. This is further evidence that the sorption of water is of a wholly different type from the usual adsorption of gases and vapors, being held as much by mutual polarization as by attachment to the charcoal.

**Summary.**—Values for the heat capacity of water, argon and hydrogen sorbed in charcoal have been utilized as evidence of the state of the sorbed substance and of the type of sorption bond. A distinction is made between the physically adsorbed gases and the persorption of water as a two-dimensional liquid film permeating the charcoal.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED DECEMBER 28, 1932
PUBLISHED JULY 6, 1933

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## A Divided Titration Pipet-Stirring Rod

BY R. RICHARDSON

The end-point of a titration is often tediously approached. This may be overcome by rapid titration followed by a back titration but this requires preparation of a second standard solution and the accuracy is reduced. In certain cases it is advisable to part the solution into two beakers, titrate one part rapidly, and from the information obtained to titrate more confidently the second portion. An adaptation of this method making use of a special stirring rod has been in use in this Laboratory for three years.

The method, while extremely simple, saves much time in precision work and has also the added benefit of making it possible to conduct titrations in many instances in a given or constant time. This has been found to increase the accuracy, as the drainage, etc., factors are constant.

The pipet-stirring rod is made of hollow glass tubing. The lower half consists of a cylindrical barrel about twice the diameter of the tubing above and having a capacity (each case has its own most suitable dimensions) of about four cc. The lower end of the barrel is drawn out to a restricted tip, small enough to reduce considerably diffusion between the contents of the