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

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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 (±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 (±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.

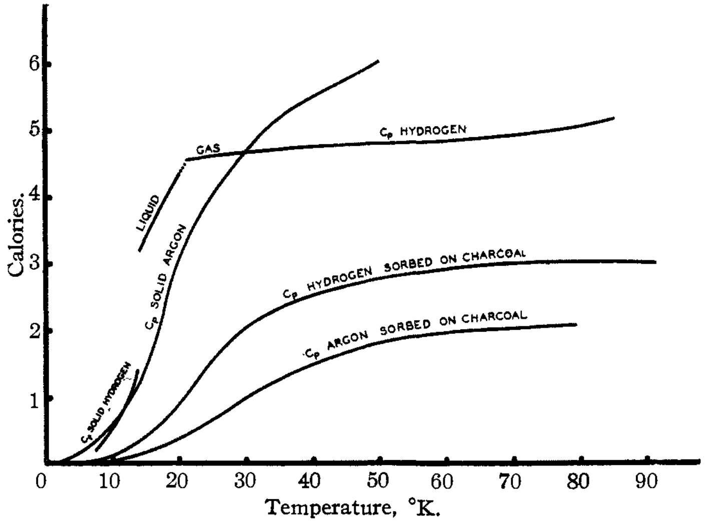

Fig. 1.—Heat capacity of argon and hydrogen in the free and sorbed state.

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

(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

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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 barrel and the surrounding liquor, but large enough to permit ready flow between them when desired. The pipet is fitted at the top with an ordinary glass stopcock, leaving a mouthpiece of glass about 2.5 cm. above the cock. Its total length is not longer than a stirring rod.

The sample to be analyzed is secured in a beaker, diluted suitably, and indicator added if necessary. The portion is adjusted when possible to require a set amount of standard solution. The stirring rod is introduced and the barrel filled. The pipet stopcock is closed and the standard solution run into the beaker as rapidly as possible from the buret to a slight excess, the buret stopcock being full open until the end-point is signaled. The pipet meanwhile functions as a stirring rod. Half of the withdrawn barrel portion is now drained into the beaker and titration repeated to excess, this time by additions of say twenty drops each. This cycle is repeated with say five drop portions. The rod is then rinsed in the solution by running liquid in and out several times. The final titration in one drop portions is rapid. The color variation or other indication of the end-point is fresh in the memory. Judgment is not strained. It was found even when duplicates were being run that it was quicker and easier to titrate by this method. A medicine dropper arrangement is similar but not satisfactory. It is not precise and not readily cleaned.

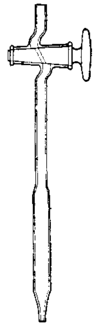
Fig. 1.—Diagram of pipet-stirring rod.

If the sample can be adjusted approximately to require a set volume of standard solution the titration (with a set procedure) will always occur in a fixed time.

CONTRIBUTION FROM THE
DEPARTMENT OF PHYSICAL CHEMISTRY
MCGILL UNIVERSITY, MONTREAL

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A New Glass Packing for Laboratory Fractionating Columns

BY C. D. WILSON, G. T. PARKER AND K. C. LAUGHLIN

A highly efficient packing suitable for general use in laboratory fractionating columns has recently been developed in this Laboratory. The packing is a glass modification of the single and double-turn wire helixes which have been used here with excellent results.

The apparatus required for making the glass coils is very simple: a brass (or other metal) rod of 3.2 mm. diameter and about 31 cm. long is equipped to hold a 2–3 mm. glass rod (by flattening a portion of the metal rod and drilling a hole or by slotting the end of the metal rod and bending the prongs to fit the glass rod). The end of a 2–3 mm. soft glass rod is inserted into this opening and heated in a moderate Bunsen flame to softening. The metal rod, held in the right hand at right angles to the glass rod, is then rotated counter-clockwise, winding the softened glass in a spiral. After starting the spiral, the metal rod should rest on and be supported by the glass rod, and be about 3.2 to 6.4 mm. from the heated tip of the glass rod. By this process, the rod can be drawn to any desired diameter by varying the rate of turning. The space separating the turns is controlled by the angle at which the metal rod is held. With a little practice a uniform glass spiral can be wound having the size of No. 22 B. and S. wire, and about 10–12 turns per cm. This is easily removed from the rod when cool, and is broken up into single and double turns, which are sorted.

Fractionating columns packed with this material (usually 75% single, 25% double turns) have found a wide application in this Laboratory. This packing is far superior to the usual 5 × 5 mm. glass tubes. The flooding tendency is less (higher vapor velocity), enabling more rapid distillation, particularly under reduced pressures. The H. E. T. P. (height equivalent to a theoretical plate) of the new packing as determined by distilling a mixture of benzene and carbon tetrachloride[1] was 1.8 inches (4.57 cm.) in a total condensation, variable take-off column[2] with a packed section of 44 × 1.4 cm. and 2.0 inches (5.08 cm) in a similar column with 40 × 0.8 cm. packed section. The H. E. T. P. with 5 × 5 mm. glass tubes in a similar 40 × 1.4 cm. column was 4.0 inches (10.2 cm.). Thus by the use of the new packing the number of theoretical plates in a column can be more than doubled, while the distillation rate is also increased.

(1) Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

(2) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

STATE COLLEGE, PENNSYLVANIA

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The Homogeneous Reaction between Hydrogen and Fluorine

BY HENRY EYRING AND LOUIS S. KASSEL

It has been reported by Moissan and Dewar[1] that immediate explosions are obtained when fluorine is brought into contact with liquid hydrogen. Since it seemed to us improbable that molecular hydrogen and molecular fluorine could react without considerable activation, we attempted to repeat this experiment. We were prevented from doing so by experimental mishaps; we did find, however, that there is no appreciable homogeneous reaction between the gases at room temperature.

Fluorine was obtained from a generator of the usual type and conducted through copper tubing to the center of a 3-liter flask. Hydrogen and nitrogen from tanks could also be admitted near the center; an exit tube also was provided. The ordinary procedure was to flush the flask out with nitrogen, and then to admit first one, then the other, of our reactant gases.

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(1) H. Moissan and J. Dewar, *Compt. rend.*, **124**, 1202 (1894); **136**, 641, 785 (1903).

Under no circumstances did we observe a steady flame where the gases mingled. Sometimes we observed flashes from the copper tubing. In other experiments there would be no reaction for several minutes, and then a rather mild explosion, sufficient merely to blow the rubber stopper out of the bulb. In one experiment, in which we had admitted hydrogen first, a much larger quantity than usual of fluorine was added with no sign of reaction; we then waited for half an hour and finally decided to sweep the mixture out with nitrogen. A rapid flow of nitrogen was started, and immediately a very violent explosion occurred; the flask was pulverized, an enclosing towel cut into shreds and a wire-in-glass safety screen cracked in a dozen places. Presumably this explosion was initiated by sulfur, talc or other catalytic material from the rubber tubing of the nitrogen supply. In any case, there must have been for half an hour preceding the explosion, a mixture varying in composition from 100% hydrogen to 100% fluorine, without appreciable reaction occurring. The ionization from cosmic rays and local radioactivity may have started some chains. Unless branching occurred, very slight amounts of reaction would result. Since the atomic chains which we expect here cannot branch, we believe that the explosions observed are of the thermal type, occurring only when sufficient energy has been liberated in some small region. It is not impossible that explosions should be produced by the "bursts" of cosmic radiation that various observers have noted, but the normal ionization is certainly ineffective.

Our results are in agreement with the observations of Wartenberg and Taylor.[2] They agree also, as was previously suggested, with our theoretical expectations; the most exact formulation of these[3] predicts for

$$H_2 + F_2 = 2HF$$

an activation energy of over 50 kcal. Reaction by way of the atoms

$$\begin{aligned} F + H_2 &= HF + H \\ H + F_2 &= HF + F \end{aligned}$$

should require little or no activation; the temperature coefficient of the thermal reaction occurring in this way should be due almost entirely to the temperature coefficient of the dissociation of fluorine; the over-all activation energy would be 30 to 40 kcal. Thus thermal reaction, by way of the atoms, should begin at 150–250°; it certainly cannot occur at liquid hydrogen temperature unless it is initiated by some very active catalyst, by discharge of static electricity, or other extraneous cause.

These experiments were made in 1930, at the University of California.

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
4800 FORBES STREET
PITTSBURGH, PENNSYLVANIA

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(2) H. N. Wartenberg and J. Taylor, *Nachr. Ges. Wiss. Göttingen. Geschäft. Mitt. Math.-physik. Klasse*, **1**, 119 (1930).

(3) H. Eyring, THIS JOURNAL, **53**, 2537 (1931).

A Paradoxical Solubility Phenomenon with Gelatin

BY CLARENCE E. LARSON AND DAVID M. GREENBERG

During the course of an experimental study of the electrochemical properties of proteins in glacial organic acids, it was noticed that, using the same stock gelatin, solutions in glacial acetic acid were sometimes readily obtained and at other times the gelatin showed very little tendency to dissolve even on heating or with vigorous and prolonged agitation. This curious behavior was finally traced to the fact that the gelatin was soluble in the acetic acid when the concentration was greater than a certain limiting level but was insoluble below this limit. In other words, gelatin in acetic acid offers the paradoxical example of a substance that is soluble in a concentrated solution but is insoluble in dilute solution. Above the limiting solubility value as far as could be judged, it was possible to prepare gelatin solutions of any concentration.

Fig. 1.—The change of the minimum solubility concentration of gelatin in acetic acid with temperature.

As might be expected, the limiting solubility value was found to vary somewhat with different samples of gelatin and also to change with the temperature, so that as the temperature was raised, a point was reached at which the gelatin became completely soluble in all proportions in the acetic acid.

The phenomenon can be most readily demonstrated by first preparing a concentrated solution of the gelatin in acetic acid and then diluting with more acetic acid. The gelatin flocculates out when it is diluted to below the limiting solubility value. This is the most convenient way of studying the subject and was used by us to determine quantitatively the limiting solubility values. The material used mostly was Eastman Kodak Company's electrolytically de-ashed gelatin with an ash of 0.035% and a moisture content of 12%. The acetic acid was Baker C. P. containing 99.5% of the acid. The curve in Fig. 1, giving the change of the lower level of solubility with temperature, was determined on this gelatin. The experiments were carried out by warming a stock solution of the gelatin and the glacial acetic acid to the desired temperature in a water-bath and then adding portions of the acid to the gelatin solution until a standard turbidity developed. This turbidity was determined using the same glass vessel in every case and adding acetic acid until the lettering of a selected printed page could no longer be distinguished through the liquid. As Fig. 1 shows, for this sample of gelatin the solubility limit was 3.1% at 20°, and at 25° 2.7%. The temperature of complete miscibility was determined as 80°.

It was suspected that the moisture content of the gelatin might be the source of this curious behavior and a certain small amount of water is required to disperse gelatin in acetic acid. However, this did not prove to be the case, since on adding up to 5% of water to the acetic acid, which is far more than is introduced with the gelatin, the phenomenon still persisted.

As a test of the reversibility of this paradoxical solubility behavior, the following experiment was carried out. A sample of gelatin thrown out from solution by diluting with acetic acid was collected, dialyzed in a collodion membrane to remove the acid, and was then flocculated from the aqueous solution with alcohol. After being thoroughly dried in a vacuum desiccator, the solubility of this recovered gelatin was tested. It was found to have the same features as the original gelatin, namely, it dissolved to form a concentrated solution and was flocculated out on being diluted with more acetic acid.

Other proteins tested by us proved to be completely insoluble in acetic acid.

DIVISION OF BIOCHEMISTRY
UNIVERSITY OF CALIFORNIA MEDICAL SCHOOL
BERKELEY, CALIFORNIA

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