Sodium nitrate has been found to undergo ammonolysis in contact with fused sodium amide, with formation of sodium trinitride. At 175° a yield as high as 65.7% has been obtained on the basis of the equation, $NaNO_3 + 3NaNH_2 = NaN_3 + 3NaOH + NH_3$.

Higher temperatures favor thermal decomposition of the sodium trinitride, which is probably formed at first in theoretical quantities.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY OF BRISTOL]

A NEW SORPTION BALANCE[1]

BY J. W. MCBAIN AND A. M. BAKR

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In a paper by the authors[2] on sorption by charcoal it was mentioned in a footnote[3] that a new and improved method had been worked out, which was capable of being applied to all measurements of sorption by solid surfaces. This paper will give the details of the construction and use of the "Sorption Balance."

The earlier method had necessitated the experiment being concluded whenever a reading was desired, so that it was not possible to observe the behavior of the same specimen of charcoal under different conditions of sorption, and it was consequently necessary to assume that different specimens of the same preparation of charcoal exhibited exactly the same properties. Though this was the case in the majority of the experiments made, it is clear that through accidental treatment the activity of the specimen might be very appreciably altered, so that it would be much more satisfactory if a whole isotherm or a complete series of isotherms could be obtained for the same specimen of sorbing material, which was not exposed to any foreign gas or vapor between the experiments.

Many attempts were made by the authors to devise an apparatus embodying these desirable features but, as all the earlier attempts with metal springs and balances of various designs failed owing to the properties of the spring undergoing permanent alteration under the temperature changes that were necessary, only the final form of the apparatus will be described.

The essential part of the apparatus consists of a spring balance, the spring being made of a fine silica fiber. The preparation of the balance will first be briefly described. Long, thin fibers of silica, about 75 to 150 cm.

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[1] The manuscript of this paper was posted by registered post on April 7, 1925, but was lost in transit (compare *Nature*, July 4, 1925, p. 14, vol. 116); it is now submitted unaltered as other laboratories have been in the meantime making extensive use of our balance as here described.

[2] Bakr and McBain, THIS JOURNAL, **46**, 2718 (1924).

[3] Ref. 1, p. 2722.

long and 0.2 mm. thick, are prepared by heating rods of silica of about 4 mm. diameter in the oxygen-coal-gas blow-pipe flame and drawing out rapidly. With a little practice it is an easy matter to prepare these fibers; of course, it is not possible to regulate the thickness with any approach to accuracy, but usually in a lot of a dozen such fibers, only one or two are found to be too thick or too fine for any kind of spring.

The rest of the treatment of the fiber is now done in the ordinary gas blow-pipe flame. The fiber is bent at right angles in a small flame, then attached to a carbon rod (by a thread or a gummed label) of the diameter desired in the finished spring, and the silica fiber is then coiled into a helix by turning the rod continuously, while the fiber is always heated at the point where it is being bent. The helix should be wound as closely as is possible, in order to approximate to the conditions for the mathematical treatment of helical springs. Finally, the ends of the spring are bent up into hooks lying in the axis of the spring, when the finished coil will appear as in the diagram.

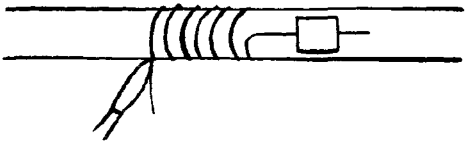

Fig. 1.—Method of bending quartz spiral.

It is necessary now to calibrate the spring to find the extension for given weights attached to the end. As the sorbent will have to be contained in a small "bucket" of some kind, usually of welded platinum or gold, it is convenient to employ this as the container for the weights to be hung from the spring during the calibration. The spring is supported from a small glass hook and the bucket then attached. The length of the coil when supporting the bucket is then read, the two ends of the spring being observed in the eyepiece of a reading or traveling microscope. Both ends of the coil having been bent so as to lie in the axis of the coil, it is unnecessary to focus the two images in the eyepiece separately, so that no error arises from any possibility of a defective focusing apparatus. A weight of 0.1 g. is put into the bucket, and the length of the spring again read. Now 0.2 g. is added, 0.3 and up to 0.5 or 0.6 g. Thus a calibration curve is obtained which is linear for a moderately sensitive spring, but departs from the linear relation for a more sensitive one owing to the large extension, and consequent departure from the condition of a "flat" helix. As the sorption experiments are probably to be made at various temperatures, the spring is calibrated at, say, four temperatures which will include the range to be employed in experimentation. The change of the extension is fairly small and is regular, so that another graph enables readings of the extensions per unit weight added to be made for the intermediate temperatures.

The rest of the apparatus is very simple; see the diagram. It consists of a straight glass tube, some 25 cm. long by 2 cm. in internal diameter, with a slight waist near the top. The liquid to be employed in the sorption is distilled in a vacuum into a thin glass bulb, which is then sealed. To the bulb is attached a small bar of iron (encased in glass to prevent any action between the liquid and the iron). The bulb and iron bar are then placed at the bottom of the tube. Next, the spring, with the bucket filled with sorbent attached, is hooked to a small glass sphere and lowered into the tube; the sphere rests on the waist, and so supports the balance. The top of the tube is now sealed. The apparatus is sealed to a high-vacuum system by the tube at the bottom, which is drawn out for sealing off. The whole upper part of the sorption apparatus is surrounded by an electric furnace (a tube wound with Nichrome wire) which will reach a temperature of about 450°, and the temperature is then gradually raised. The tube is tilted slightly so that the bucket rests on the slide and is heated directly, and the spring is relieved of shocks during the evacuation and sealing. When the furnace has reached its highest temperature slow evacuation by the water pump is commenced; after this latter has attained its maximum vacuum a "Cenco" oil pump is started up slowly and, finally, a mercury-vapor pump capable of producing a vacuum of the order of 10^{-5} mm. If the evacuation be started before the heating of the charcoal, or if it be too rapid, quite suddenly the greater part of the charcoal will leave the bucket owing to the rapidity with which gas is evolved. After evacuation at this temperature and high vacuum for some four or five hours, the tube is sealed from the pump.[4] The complete apparatus is now a small self-contained unit and it is not opened again until the investigation has been completed.

The lower part of the tube is next placed in a freezing mixture of carbon dioxide and ether, or liquid air, and if the bulb containing the liquid has not broken owing to expansion on freezing or liquid tension on cooling (if there was no vapor in the bulb at the start) it is broken by raising with an electromagnet and then allowing it to fall. It is necessary that the liquid should be at a low temperature and so possess a vapor pressure of not more than a few hundredths of a millimeter, or the bucket will be blown off the spring by the upward rush of vapor.

The sorption may now be measured under any desired conditions. The upper part of the tube is enclosed in an electric thermostat at whatever temperature it is desired to measure the sorption, while the pressure of

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[4] An important improvement is to evacuate through the upper end and to have at the bottom a further compartment containing a bulb full of the liquid. This bulb is broken after thorough evacuation and the vapor is allowed to condense upon the sorbent, displacing other tenaciously retained impurities. The heating and evacuation is now repeated and the auxilliary tube at the bottom sealed off and removed. By this method of cleaning the surface of the sorbent much greater sorption may often be attained, and even the whole form of the sorption curve changed. It is evident that most of the published data on sorption are affected by neglect of this source of error.

the vapor in contact with the sorbent is regulated by placing the lower end of the tube in another thermostat. See the diagram of the completely assembled sorption unit.

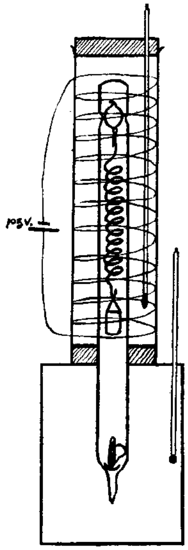

Fig. 2.—The sorption balance in superposed adjustable thermostats.

The diagram illustrates a simple kind of thermostat employed for many single experiments, which is very satisfactory; for further experiments large glass-fronted, automatically regulated ovens are being used.

It is, of course, necessary that the vapor pressure of the liquid used should be known over the range of temperature for the lower bath. It will be obvious that with this apparatus we are enabled to return to lower pressures of vapor over sorbent, or to any isotherm, and also to approach an equilibrium from both sides in successive experiments without exposing the sorbent to any other gas or vapor in the interval. The sorption unit need not be opened until the complete series of isotherms has been secured.

There is a further improvement that can be attained. So far, it has not been possible to make experiments with different vapors on the same specimen of charcoal, but a slight modification of the apparatus will allow this to be done without exposing the charcoal between the experiments.

The principle of the sorption balance is not limited to experiments with volatile liquids, and preliminary experiments with the permanent and semipermanent gases up to pressures above 30 atmospheres have already been effected.

Apart from its extreme simplicity, another advantage of the sorption balance is that the process of sorption can be watched by the movement of the lower end—the top end is stationary—of the spring in the eyepiece of the microscope. Apparently, the greater part of the sorbed material is taken up very rapidly.

Experimental Part

Springs.—Below is given a typical calibration (by H. G. Smith) for a sensitive spring; extension, 9 cm. per 1 g. of added weight.

The dimensions of the spring are as follows: fiber, 0.02 cm. in diameter; coils, 1.25 cm. in diameter. The number of coils was 15; the length of spring with no weight attached was 5.986 cm.

The values in the columns on the right represent the increase in length on adding the final 0.1 g., the total weight suspended being given in the first column. The weight of this platinum bucket was 0.2019 g., and its capacity was approximately 0.5 g. of charcoal.

The sensitivity of a spring depends very much on the diameter of the

TABLE I

A TYPICAL CALIBRATION

Extension on addition of 0.1 g.

Spring + added wt.	32°	80°	165°	265°
None	5.986	5.986	5.986	5.986
Bucket	7.968	7.962	7.937	7.917
0.1 g.	0.947			
.2 g.	.920			
.3 g.	.919			
.4 g.	.907	3.672[a]	3.635[a]	3.598[a]
.5 g.	.900	0.893	0.883	0.876
.6 g.	.890	.889	...	...

[a] Total increase in length for first 0.4 g.

coils, since the third power of the diameter is involved in the extension. Some large coils of 2 cm. diameter have been used for the determination of very small quantities of sorbed substance.[5]

In general, a value of 4cm. extension per gram has been regarded as a minimum permissible sensitivity.

Accuracy.—The lengths of the springs under various loads are read with a traveling microscope to 0.001 cm., giving a total error in the length for a single reading of 0.002 cm. For the spring used in the calibration given above this corresponds to a weight of approximately 2.10^{-4} g.

The weight that may be placed in the bucket is about 0.5 g. so that the error represents less than 0.05% of the weight of sorbent. For sorption by charcoal the weight of sorbed substance in preliminary experiments appears to vary between 7 and 30% of the weight of the sorbent for different vapors and, hence, the error in the determination of the weight of the sorbed substance to the sorbent (x/m) will lie inside the limits 0.75 to 0.15%. This is a good order of accuracy to obtain in measurements of this type, and of course can be indefinitely increased by the use of longer and springs of larger diameter at the expense of making the apparatus larger.

Applications and Summary

It is clear that the use of the sorption balance constitutes one of the most convenient and accurate methods for the measurement of the sorption of gases and vapors on solid surfaces over the widest range of experimental conditions of temperature and pressure. Where the critical pressure and temperature are not too high, investigation of the sorption may readily be made below and above the critical point, thus providing data that should be of great value in testing current theories of the state of matter sorbed on solid surfaces. The sorption balance is already being applied, for example, to such diverse experiments as the sorption of vapors and gases on charcoal, sorption by crystalline surfaces, the sorption of moisture by

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[5] In these long coils two or more fibers are joined in the oxygen blow-pipe flame.

various types of building materials, of different classes of volatile liquids by nitro-cotton, and should be applicable to some hydration phenomena and even to determination of molecular weight in small quantities of solutions.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY OF THE UNITED STATES DEPARTMENT OF AGRICULTURE]

THE THERMAL DISSOCIATION OF SODIUM CYANIDE

BY E. W. GUERNSEY AND M. S. SHERMAN

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It has been recently shown[1] that the fixation of nitrogen as cyanides, usually represented by the equation,

$$Na_2CO_3 + N_2 + 4C \rightleftharpoons 2NaCN + 3CO \qquad (1)$$

takes place, at least to a large extent, through the following series of reactions.

$$Na_2CO_3 \rightleftharpoons Na_2O + CO_2 \qquad (2)$$

$$(C + CO_2 \rightleftharpoons 2CO) \qquad (3)$$

$$Na_2O + C \rightleftharpoons 2Na + CO \qquad (4)$$

$$2Na + 2C \rightleftharpoons Na_2C_2 \qquad (5)$$

$$Na_2C_2 + N_2 \rightleftharpoons 2NaCN \qquad (6)$$

The "over-all" equilibrium represented by Equation 1 was studied by Ferguson and Manning[2] and later by Ingold and Wilson[3] with somewhat different results. A few measurements were made in this Laboratory in conjunction with the present investigation and the results were found to agree more closely with those of Ingold and Wilson. It is, therefore, believed that the relation which they deduced for the variation in the composition of the Na_2CO_3-NaCN melt with the composition of the gas phase is at least fairly accurate. It will be seen, however, that the study of this "over-all" equilibrium does not give us as much information on the state of the system as would be desirable if the intermediate substances such as sodium oxide, sodium carbide or sodium are present at equilibrium in significant amounts.

It has been found that for a given ratio of nitrogen to carbon monoxide in the gases, the ratio of sodium cyanide to sodium carbonate in the molten phase increases rapidly with increasing temperature, so that according to the equation of Ingold and Wilson,

$$\log\left(\frac{x^2}{1-x}\cdot\frac{P^3_{CO}}{P_{N_2}}\right) = 23.91 - \frac{31738}{T}$$

the conversion of carbonate to cyanide should be 95% complete when the gas phase is 75% carbon monoxide and the temperature 1100°. It might,

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[1] THIS JOURNAL, **47**, 1932 (1925).

[2] Ferguson and Manning, *J. Ind. Eng. Chem.*, **11**, 946 (1919).

[3] Ingold and Wilson, *J. Chem. Soc.*, **121**, 2278 (1922).