

Summary

1. An improved type of rotating adiabatic calorimeter is described with which heats of solution or heats of dilution may be determined with high accuracy using only small quantities of material. The apparatus is constructed so that the solute, before solution, is not exposed to the vapor of the solvent.

2. Heats of solution of sodium chloride were determined at 20° over the whole range of concentrations.

3. An indirect but accurate method of determining specific heats of solutions is described, in which the specific heats are calculated from the temperature coefficient of the heats of solution.

4. From the heats of solution of sodium chloride at 20°, and those determined previously at 25°, the specific heats of sodium chloride solutions were calculated with an accuracy perhaps of 0.05% over the whole range of concentrations.

5. The heat of solution of finely divided sodium chloride was determined directly and from the difference between its heat of solution and that of the coarse salt, the surface energy of solid sodium chloride was calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF MERCURY VAPOR BY CHARCOAL

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In most arrangements for measuring gas adsorption, the adsorbent is constantly exposed to the vapor of mercury in pumps, manometers, etc., but it is tacitly assumed that no mercury is adsorbed. Sufficient grounds for this assumption are not evident. In general, vapors are more copiously adsorbed, the smaller the vapor pressures and molecular volumes of their liquids, the latter influence being particularly strong when the vapor is nearly saturated. On this basis, one would predict that mercury vapor would be more readily adsorbed than any other vapor or gas usually present, and that in the presence of liquid mercury at the same temperature, a sample of ordinary activated charcoal would take up several times its own weight. It is true that the pressure of mercury vapor in the system is generally very low; but this would merely delay, not prevent, adsorption, and in the course of a prolonged experiment there would be opportunity for considerable quantities of mercury to reach the adsorbent.

Certainly no such great adsorption occurs, and this is intimately connected with the fact that mercury does not wet charcoal. This means not that there is no attraction of the carbon surface for mercury atoms, but that this attraction is less than that of the free mercury surface, so that

the transfer of mercury from liquid to charcoal is endothermic. It should therefore occur, if at all, at high temperatures.

A preliminary investigation was made to see whether any adsorption could be detected at high temperatures. Three and five-tenths g. of activated coconut charcoal was suspended from a McBain¹ quartz spring balance, which had at 100° a sensibility of 5.45 mm. per g., and could be read, under the given conditions, to ± 0.005 mm., or about 0.3 mg. per g. of charcoal. At the higher temperatures used, the elasticity of the spring may have slightly increased, but the results did not seem to be sufficiently precise to make necessary the determination of a correction for this effect. Spring and load were hung in a wide glass tube closed at the top and connected at the bottom to a narrow vertical tube through which the system could be exhausted or mercury introduced from a leveling bulb. The wide tube and part of the narrow tube were kept at the desired temperature either by a vapor-bath (100, 218 and 306°) or by an electric furnace. The temperature of the latter was 480° as indicated by a pyrometer in which not much confidence was placed, although it was calibrated and found correct at 445°. A sharp temperature gradient thus existed in the narrow tube where it emerged from bath or furnace. In working at the higher temperatures, mercury was allowed to run in slowly until the meniscus reached a temperature at which the pressure of its vapor just balanced that due to the height of the leveling bulb. The pressure was estimated from the difference in levels, neglecting the expansion of the short column of heated mercury. It was found that the extension of the spring was proportional to the pressure, within the limits of error, showing that Henry's law holds, and that equilibrium was practically instantaneous. At the lower temperatures the pressure could not be safely found by this means; mercury was therefore allowed to enter the wide tube, and the pressure taken equal to the vapor pressure of mercury at the given temperature. No test of Henry's law could be made.

TABLE I

OBSERVED ADSORPTION OF MERCURY VAPOR							
Temp., °C.	Press., mm.	Adsorption mg. per g.	<i>P/a</i>	Temp., °C.	Press., mm.	Adsorption mg. per g.	<i>P/a</i>
480	420	8.8	48	218	31.5	15.9	2.0
	730	16.2	45		31.5	16.8	1.9
	420	8.8	48			Av.	1.95
	220	4.5	49	100	0.28	2.7	0.11
		Av.	47			Av.	0.11
306	100	14.5	6.9				
	175	23.4	7.5				
	100	14.0	7.1				
	200	27.1	7.4				
		Av.		7.2			

¹ McBain and Bakr, THIS JOURNAL, 48, 690 (1926).

The experimental results are displayed in Table I. Col. 3 shows the amounts adsorbed, in milligrams per gram of charcoal; Col. 4 gives the ratio of pressure to amount adsorbed. Assuming Henry's law to be valid at all temperatures, this may also be regarded as the isostere for a constant concentration of 1 mg. per g. of charcoal.

In Fig. 1, the logarithms of the average values of P/a are plotted in the usual manner against the reciprocal temperatures, and fall as well as could be expected upon a straight line, the 1 mg. isostere. On the basis of Henry's law, other isosteres have been calculated and plotted, as well as the vapor pressure of liquid mercury. The slope of the isosteres leads

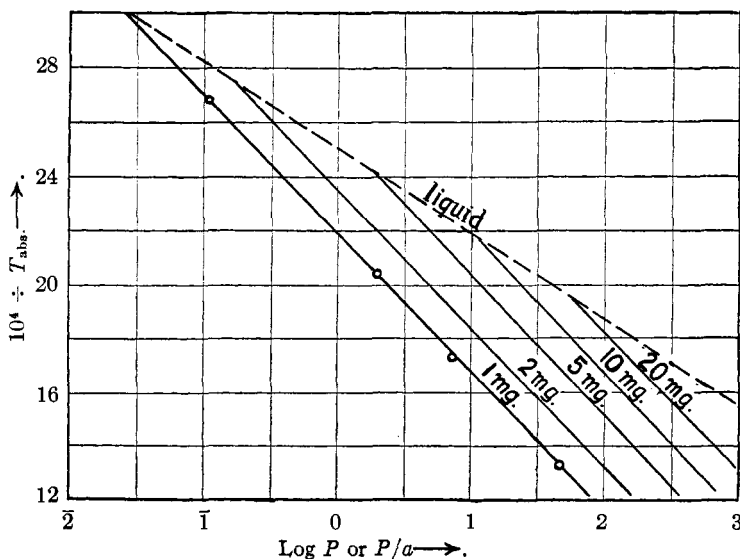


Fig. 1.

to a calculated heat of adsorption of 8900 calories per mole, which is much less than the heat of evaporation, 13,000 calories. While the transfer of mercury from gas phase at constant pressure to charcoal is exothermic and favored by low temperature, the transfer from liquid mercury to charcoal is seen to be indeed endothermic, consuming some 4000 calories, and taking place more readily at higher temperatures. The situation is similar to that which I found to exist in the case of ice and charcoal,² and is precisely analogous to the retrograde solubility of certain liquid pairs. It does not appear to have been previously described in the case of the adsorption of the vapor of a liquid.

If charcoal adsorbing a certain quantity of mercury is cooled, the vapor pressure of liquid mercury at the same temperature will fall faster than

² Coolidge, *THIS JOURNAL*, 49, 708 (1927).

the equilibrium pressure of the given mixture, and at a certain temperature will overtake it; at this temperature the system will be saturated, that is, in equilibrium with liquid mercury. The relation between this temperature and the amount adsorbed is shown in Table II (still assuming Henry's law). If the system is further cooled, its equilibrium pressure, though diminished, will now exceed the vapor pressure of the liquid, so that mercury will be desorbed and will collect as free liquid. The values in Table II therefore represent the maximum possible adsorption at the given temperatures. Evidently, there will be no significant adsorption under the conditions usually prevalent in work on other gases.

TABLE II
MAXIMUM ADSORPTION OF MERCURY VAPOR

Temp., °C.,	Vap. press. of liq. Hg, mm.	P/a	α_{\max} mg. per g.	Temp., °C.,	Vap. press. of liq. Hg, mm.	P/a	α_{\max} mg. per g.
20	0.0013	0.0042	0.3	220	33.7	2.04	16
60	.03	.026	1.2	260	98	4.0	24
100	.28	.11	2.5	400	246	7.2	34
140	1.85	.35	5.3	360	790	11.5	69
180	9.2	.89	10				

The heat of adsorption of mercury vapor, although less than its heat of evaporation, is still greater than the heat of adsorption of many true gases, and mercury vapor might therefore well be able to displace such gases from charcoal. This may be the explanation of a phenomenon which was repeatedly observed. When coconut charcoal which had been only briefly evacuated was treated with mercury vapor for three minutes, a considerable quantity of permanent gas was found in the system after all of the mercury had been condensed out. The same effect was obtained with sugar charcoal which had adsorbed formic acid, and had been only briefly evacuated. In this case the gas was doubtless carbon monoxide. The amount of gas evolved was much greater than would have come off spontaneously in a vacuum in the same time. In both cases the effect ceased when the charcoal had been subjected to prolonged evacuation.

Summary

Charcoal has been found to adsorb small amounts of mercury vapor at high temperatures. The amount adsorbed decreases with rising temperature when the vapor is kept at constant pressure, but increases with rising temperature when the vapor is kept saturated. The heat of adsorption is smaller than the heat of evaporation. At room temperature the adsorption is negligible.

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