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Abstract

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Heat Capacity of the Adsorption System Silica Gel–Water

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Physical Chemistry

The theory of adsorption equilibria is based on concepts concerning the state of adsorption complexes (^{1,2}). Along with calculations of potential curves (^{3}) and determinations of infrared spectra (^{4}), the study of the thermodynamic properties of adsorption systems, in particular their heat capacities, is of great importance for solving these problems. For the quantitative calculation of entropies, determinations of heat capacities from the lowest possible temperatures are needed. This has been done only for a few simple cases (^{5}). However, investigations of the heat capacities of adsorption systems at ordinary temperatures and at different fillings are also of great interest, since heat capacity is often very sensitive to the state of a substance. In addition, heat-capacity measurements make it possible to judge the change in the heat of adsorption with temperature.

The dependence of heat capacity on filling at ordinary temperature was determined only for the adsorption of water in porous crystals (^{6}): with increasing filling it gradually decreased by approximately 30 cal/mol • deg. However, the accuracy of determining the mean molar values of the heat capacities in (^{6}) was comparatively low: it ranged from 20 to 2%. Since we set ourselves the task of determining heat capacities at small amounts of adsorbate, it was necessary to create a calorimeter with high sensitivity and reliability of measurements.

The relative method of accurately measuring the heat capacity of both liquids and solids (^{7}) does not require measurements of the amount of heat introduced or of temperature changes; the latter usually makes the main contribution to the error in heat-capacity measurements. Method (^{7}) combines the advantages of continuous heating (^{8}) and of a differential calorimeter (^{9}). It is based on equalizing the heating rates of two bodies with known and with the heat capacities to be determined, C_1 and C_2. These bodies are heated under adiabatic conditions by heaters R_1 and R_2 (Fig. 1a). Adjustment of the resistances R_1' or R_2' makes it possible to obtain equal heating rates when

$$W_1/W_2 = C_1/C_2, \tag{1}$$

where W_1 and W_2 are the powers of the heaters. It follows from (1) that

$$\frac{C_1}{R_1}\left(1 + R_1/R_1'\right)^2 = \frac{C_2}{R_2}\left(1 + R_2/R_2'\right)^2. \tag{2}$$

Fig. 1. a —schematic of the calorimeter, b —examples of the variation of R_1' with temperature

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If (1) is not satisfied, a temperature difference arises between the two bodies. By changing R_1', it can be kept very small.

The calorimeter (Fig. 1) consists of a copper sleeve with partitions and adsorbent 1 with a total heat capacity C_2, and a massive brass cylinder 2 with heat capacity C_1. The appearance of a temperature difference between the sleeve and the jacket is detected by four spiral batteries of copper—constantan thermocouples 3 (^{10}), having 1000 junctions with a sensitivity of 10^{-6} deg. Cylinder 2 is the reference body C_1, and also the adiabatic jacket of sleeve 1.

The calorimeter is placed in an air chamber 4, whose temperature, by means of an analogous thermobattery 5 and heater 6, is maintained equal to the temperature of the shell. The optimum heating rate is 4° per hour. In all experiments R_1' was varied, i.e., the heating rate of the brass shell C_1, which rapidly acquires a constant temperature field. The cartridge with the adsorbent has poorer thermal conductivity; therefore, in order to maintain a constant temperature field, the current in it was kept constant— —by means of a PPTN potentiometer connected to points a, b, and a resistance box 8 connected in parallel with the standard resistance 7.

Fig. 1. *a* —schematic of the calorimeter, *b* —examples of the variation of R_1' with temperature

To determine the unknown heat capacity C_2 from (2), it is necessary to know the ratio C_1/R_1. For this purpose the calorimeter was calibrated when filled with substances of precisely known heat capacity. The value of C_1/R_1, obtained with different fillings of mercury, was checked by measuring the heat capacity of KCl, which proved to be 0.1621 $\mathrm{cal/mol \cdot deg}$ (according to (11), 0.1623 ± 0.0006). Before beginning measurements of the heat capacity of the adsorption system, the calorimeter was calibrated once more from 25 to 30° when filled with water.

The results of measurements of R_1' for four such experiments are shown in Fig. 1b. In this case R_2' did not change. From the values of R_1' and R_2', C_1/R_1 was calculated from (2) as a function of temperature. The subsequent calculations were made for 27°.

For the first investigation we used an adsorbent with a large specific surface area —fine-pored silica gel No. 8$^{(12)}$—and, as an adsorbate, water, which is strongly adsorbed on the hydrated surface of silica. Silica gel in the amount of 53.56 g was placed in cartridge 1 and evacuated at 110° for 45 hours. The heat capacity of silica gel was $c_c = 0.206$ $\mathrm{cal/g \cdot deg}$, which is 10% higher than the heat capacity of quartz $^{(3)}$, in accordance with the dispersity and disordered structure of the

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

particles forming the silica-gel framework and with hydration of their surface. Water was supplied to the cartridge by evaporating it

from a vacuum microburette (14). After each adsorption or desorption, the system was allowed to stand until equilibrium was reached (at small fillings—for days, at large ones for 10-12 h), after which the equilibrium relative vapor pressure p/p_s was determined and heating was begun.

Thus, in parallel, the dependence of the heat capacity was measured both on the adsorbed amount a and on p/p_s, and, consequently, the adsorption isotherm as well. The correction for absorption of the heat of desorption during heating did not exceed 1% of the heat capacity of the adsorbate. The accuracy of the measurements of the total heat capacity of the sleeve, adsorbent, and adsorbate was no worse than 0.05%.

Fig. 2. Change in the heat capacity c of the calorimetric system with increasing adsorption of water a. I—dependence of c on a; II—dependence of c on p/p_s; III —adsorption isotherm. 1 and 2—different series of measurements. Black points —desorption.

Figure 2 gives the dependence of the heat capacity of the sleeve with silica gel and adsorbed water c on a and on p/p_s, as well as the adsorption isotherm. The heat capacity exceeds the sum of the heat capacities of silica gel and liquid water. The heat-capacity isotherm is at first reversible; then it exhibits hysteresis similar to the hysteresis on the adsorption isotherm.

Figure 3a shows the dependence, on filling a, of the mean molar heat capacity of the adsorbed water

$$\bar{c}_m = (c_2 - c_r - c_c)/a,$$

where c_r is the heat capacity of the sleeve (17.636 cal/deg), and c_c is the heat capacity of the silica gel (11.154 cal/deg). It was assumed that c_c does not depend on a, i.e., the deviation of the heat capacity of the adsorption system from the sum of the heat capacities of dry silica gel c_c and liquid water $c_l = 18a$ cal/deg is associated only with a change in the heat capacity of the water.

Fig. 3. Dependence of the heat capacity of adsorbed water on filling. a—mean molar heat capacity $\bar{c}_m$; b—adsorption isotherm; c—differential molar heat capacity c_a.

Fig. 4. Dependence of the heat capacity of water on pressure. The dotted branch is obtained from Fig. 3a, b; the continuous branch is plotted according to ([17]).

Figure 4: Fig. 4. Dependence of the heat capacity of water on pressure. The dotted branch is obtained from Fig. 3a, b; the continuous branch is plotted according to ([17]).

It is seen from Fig. 3a that $\bar{c}_m$, as in (6), is everywhere greater than 18; moreover, with increasing a, $\bar{c}_m$ at first falls rapidly from very large values, then more slowly, and at saturation $\bar{c}_m$ becomes practically equal to 18, i.e., to the heat capacity of liquid water. This is connected with the complex dependence on a of the differential heat capacity of adsorbed water

$$c_a = \partial c / \partial a$$

(Fig. 3c).

As a increases, this quantity passes through a minimum in the negative region; integration of the curve $c_a = f(a)$ leads to a value close to 18.0 cal/mol · deg, i.e., the state of water in the pores at $p/p_s = 1$ is close to the state of a normal liquid.

In Fig. 3 and 2 III, the adsorption isotherm is given for comparison. Since the heat-capacity hysteresis is evidently associated with capillary-condensation hysteresis, it was of interest to relate the increase of $\bar{c}_m$ with decreasing p/p_s (or a) to the change in the negative pressure P acting on the liquid in the pores, due to the concave menisci at the mouths of pores emerging onto the surface of the silica-gel grains ([15]).

In Fig. 2 III and 3 the quantities are shown

$$P \approx \frac{\Delta\mu}{v_m} = \frac{RT \ln p/p_s}{v_m} \tag{16}$$

where $\Delta\mu$ is the change in chemical potential, and v_m is the molar volume of the liquid, assumed not to depend on P.

In Fig. 4 the dependence of $\bar{c}_m$ on the negative P obtained from this is presented. The adsorption and desorption points here fall on one curve. The continuation of this branch of the curve of the dependence of heat capacity on the stretching of the liquid is the branch expressing the dependence of heat capacity on its compression in the region of positive P, constructed according to ([17]).

Fig. 4. Dependence of the heat capacity of water on pressure. The dotted branch is obtained from Fig. 3a, b; the continuous branch is plotted according to ([17]).

Thus, heat-capacity measurements show that the state of the sorbate in the pores in this region does indeed correspond to a strongly stretched liquid*.

We note that the phenomenon of capillary condensation makes it possible to measure the heat capacity of a liquid under large negative pressures.

The high values of $\bar{c}_m$ at small a apparently correspond to considerable freedom of vibrations and migrations of water molecules in adsorption complexes formed on the surface of silica.

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REFERENCES

1. A. V. Kiselev, *Vestn. AN SSSR*, No. 10, 43 (1957).
2. A. V. Kiselev, D. P. Poshkus, *DAN*, **132**, 876 (1960).
3. N. N. Avgul' , A. V. Kiselev, I. A. Lygina, D. P. Poshkus, *Izv. AN SSSR, OKhN*, 1957, 1314; 1959, 1196.
4. A. V. Kiselev, V. I. Lygin, *Koll. zhurn.*, **22**, 403 (1960); **23**,
5. L. E. Drain, J. A. Morrison, *Trans. Farad. Soc.*, **49**, 654 (1953).
6. G. L. Kington, *The Structure and Properties of Porous Materials*, Ed. D. Everett, F. Stone, London, 1958, p. 247.
7. G. I. Berezin, *Izv. AN SSSR, OKhN*, 1959, 1143.
8. M. M. Popov, G. L. Gal' chenko, *ZhOKh*, **21**, 2220 (1951).
9. T. W. Richards, J. T. Gucker, *J. Am. Chem. Soc.*, **47**, 1876 (1925).
10. G. I. Berezin, *Zav. labor.*, No. 4, 484 (1959).
11. M. M. Popov, *Thermometry and Calorimetry*, Moscow State University Press, 1954.
12. O. M. Dzhigit, A. V. Kiselev, I. E. Neimark, *ZhFKh*, **28**, 1804 (1954); L. D. Belyakova, O. M. Dzhigit, A. V. Kiselev, ibid., **31**, 1577 (1957).

13. *Handbook of Chemistry and Physics*, 37th ed., 1955–1956, Chem. Rubber Publish. Co.

14. O. M. Dzhigit, A. V. Kiselev, G. G. Mutik, *Koll. zhurn.*, **23**.

15. A. A. Isirikyan, A. V. Kiselev, *ZhFKh*, **32**, 679 (1958).

16. A. V. Kiselev, *Proc. Second Internat. Congress on Surface Activity*, **2**, London, 1957, p. 189.

17. P. S. Epshtein, *Course of Thermodynamics*, Moscow, 1948.

* This previously made it possible to explain the maxima of the heats of completion of the heats of capillary condensation ([14,15]).

Note: Figure translations are in progress. See original paper for figures.

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