At the lower temperature the resistance decreased by over a per cent. in a field of 8490 gauss. A negative magnetic coefficient of resistance has been observed previously only in the case of ferromagnetic metals.

BERKELEY, CALIF. RECEIVED OCTOBER 29, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

An Experiment on the Adsorption of Helium Gas Used for Thermal Conduction in Calorimetry near 1°K. The Heat of Adsorption

BY J. W. STOUT AND W. F. GIAUQUE

In the course of their adiabatic demagnetization experiments, Giauque and MacDougall[1] determined the order of magnitude of the amount of helium gas which should be added to a calorimeter to ensure the best possible gas conduction without introducing undesirable heat effects caused by the helium. The principal heat effect is due to the condensation of helium rather than to the heat capacity of gas. The present experiment was not intended to yield very precise or extensive results but rather to help provide a better sense of proportion as to adsorption phenomena occurring in a calorimeter at these temperatures.

Most of the substances which have proved of interest in the adiabatic demagnetization experiments are hydrated salts and the presence of some excess water is ordinarily not objectionable. Thus a typical situation is a calorimeter filled with moist crystals and the adsorption phenomena may well be characteristic of ice rather than of the substance investigated. Although nickel sulfate heptahydrate is not suitable for producing temperatures below 1°K., we happened, in connection with another investigation, to have a convenient opportunity of investigating the adsorption of helium in a sample tube filled with moist crystals of this material. As it appears probable that the results are typical, it seems desirable to present them here.

Seventy-eight grams of $NiSO_4 \cdot 7H_2O$ was broken up until it would pass through a screen with holes 0.5 mm. square. This procedure was to prepare the crystals for other experiments to be reported elsewhere. The crystals were then placed in a saturated solution of nickel sulfate and allowed to stand for three hours to eliminate rough surfaces from the broken crystals. They were then removed from the solution and dried until there was about 0.2 mole of excess water per mole of $NiSO_4 \cdot 7H_2O$. An examination of the crystals under a microscope showed that the average diameter was about 0.25 mm. The crystals were placed in a 62.7-cc. Pyrex glass sample tube which was connected to a McLeod gage measuring system and could be immersed in a liquid helium bath. A known amount of helium gas was added to the sample tube system and line volumes and their temperatures were known with sufficient accuracy to permit calculation of the amount of adsorbed helium at any time.

The experiment was performed in a Dewar flask of about eight liters capacity which was nearly full of liquid helium. As the chronological order in the experiment is of interest the details are recorded in Table I.

The surface area of the crystals was estimated to be about 10,000 sq. cm. and, using the density data on liquid helium to make an estimate of the area occupied by a helium atom, it is found that about 1.3×10^{-5} mole would produce a monomolecular layer on the surface.

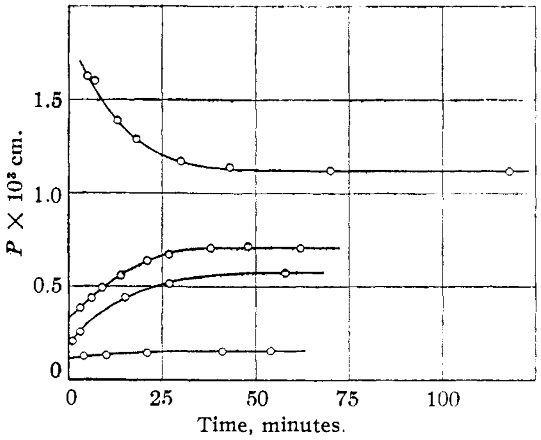

Fig. 1.—Adsorption pressure of helium gas on $NiSO_4 \cdot 7H_2O$ at 4.23°K.

The data at 4.23°K. are shown in Fig. 1, where it is evident that fairly complete equilibrium is obtained in about an hour.

It is of interest to estimate the heat of adsorption with the assistance of the Sackur–Tetrode equation. In making this calculation we will make use of the fact that liquid helium has a

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[1] (a) Giauque and MacDougall, THIS JOURNAL, **57**, 1175 (1935); (b) MacDougall and Giauque, *ibid.*, **58**, 1032 (1936).

TABLE I

DATA RELATING TO THE ADSORPTION OF HELIUM

11:40 A. M. Sample tube had attained a temperature of 4.23°K. with helium gas present.

12:20 P. M. A small amount of helium was pumped out and the pressure allowed to increase at the expense of adsorbed helium.

	$P \times 10^4$ cm.		$P \times 10^4$ cm.
12:24	1.26	1:01	1.51
30	1.30	14	1.54
41	1.45		

1:15 to 3:00. During this interval the liquid helium bath was at various reduced pressures. The adsorption pressure decreased but the measurements did not correspond to equilibrium and are not recorded here. Also during this interval a small amount of helium gas was added to the sample tube.

3:06 to 5:15. During this interval the temperature was constant at about 1.35°K.

	$P \times 10^4$ cm.		$P \times 10^5$ cm.
3:06	4.49	4:20	9.0
13	3.94	30	7.1
25	2.84	40	6.3
37	1.95	50	5.5
51	1.58	5:01	4.9
4:01	1.16	15	4.7

5:16. Liquid helium was added to the Dewar vessel with a large stirring effect and the temperature was raised to 4.23°K.

	$P \times 10^3$ cm.		$P \times 10^3$ cm.
5:21	1.62	5:46	1.17
23	1.60	59	1.14
29	1.39	6:26	1.12
34	1.29	7:12	1.12

7:15. A small amount of helium gas was pumped from the sample tube and the pressure allowed to increase at the expense of adsorbed helium.

	$P \times 10^4$ cm.		$P \times 10^4$ cm.
7:18	3.83	7:42	6.70
21	4.33	53	7.05
24	4.92	8:03	7.17
29	5.55	17	7.05
36	6.34		

8:20. A small amount of helium gas was pumped from the sample tube and the pressure allowed to increase at the expense of adsorbed helium.

	$P \times 10^4$ cm.		$P \times 10^4$ cm.
8:21	2.08	8:47	5.12
24	2.56	9:18	5.75
35	4.41		

Adsorption observations could have been continued easily for several days with the one liquefaction of helium but in this case the liquid was to be used for another experiment so the adsorption measurements were discontinued at 9:18 P. M.

The amount of helium on the surface at various times was as follows.

Time	T, °K.	Amount in moles	Equil. P cm.
1:14	4.23	1.32×10^{-5}	1.6×10^{-4}
5:15	1.35	2.07×10^{-5}	....
7:12	4.23	1.75×10^{-5}	1.12×10^{-3}
8:17	4.23	1.69×10^{-5}	7.1×10^{-4}
9:18	4.23	1.61×10^{-5}	5.8×10^{-4}

negligible entropy below 2°K. and it is undoubtedly safe to assume that the adsorbed helium has a negligible entropy at 4°K.

$$\Delta S = S_{\text{gas}} = R \ln \frac{M^{3/2} T^{5/2}}{P} - 2.300 \qquad (1)$$

where P is in atmospheres. When P is the equilibrium pressure, $\Delta H = T\Delta S$.

The heat of adsorption was found to be 131, 135, 137 and 148 cal./mole for the equilibrium pressures 1.12×10^{-3}, 7.1×10^{-4}, 5.8×10^{-4} and 1.6×10^{-4} cm., respectively, all at 4.23°K. These values may be compared with the heat of vaporization of helium which is about 20 cal. per mole.

From the heat of adsorption of the helium the equilibrium pressure may be calculated as a function of temperature. With the amount of helium giving an equilibrium pressure of 1.12×10^{-3} cm. at 4.23°K., it is found that the equilibrium pressure would be 8×10^{-17} cm. at 1.35°K. Thus the maintenance of the observed pressures at 1.35°K. is due only to slow rate in attaining the type of adsorption characteristic of the 4.23° observations. The measurements at 1.35°K. were made with a small excess of helium on the surface over the amount corresponding to the 4.23° value but this should not change the significance of the order of magnitude.

The series of measurements beginning at 5:21 P. M. offers additional evidence that equilibrium with respect to the type of adsorption characteristic of the measurements at 4.23° had not been attained at the lower temperature. Before this series the sample had been warmed suddenly from 1.35 to 4.23°. The pressure increased from 4.7×10^{-5} cm. at the low temperature to 1.62×10^{-3} cm. at 4.23°. It then slowly decreased and approached the equilibrium value of 1.12×10^{-3} cm.

However, the helium responsible for the observed pressures at 1.35° was adsorbed in what may be considered an unstable secondary manner and it is of interest to inquire into the order of magnitude of the heat evolved in this type of adsorption.

Again making use of equation (1) and the observed pressures 4.49×10^{-4} and 4.7×10^{-5} cm., at the beginning and end of the series, the heats of adsorption are found to be 37 and 43 cal. per mole, respectively. It is not to be supposed that this magnitude is characteristic of more than a very small amount of the adsorbed helium but it is this amount that is of particular interest in connection with the establishment of pressures suitable for the gaseous conduction of heat. From the approximate 40 cal. value for the molal heat of adsorption it may be seen that the forces holding the helium atoms are not of a much different magnitude than those existing in liquid helium.

It seems highly probable that when a calorimeter is suddenly cooled to temperatures below a degree, the approach to true adsorption equilibrium would occur very slowly and that the situation characterizing the condensed helium would resemble even more closely the conditions existing in liquid helium. In fact, considering the great change between 4.23 and 1.35°, we expect that the remaining pressure in a calorimeter at several tenths of a degree absolute will not differ greatly from that calculable for liquid helium. At the same time it is evident that an investigation extending over a day or two with the calorimeter often at, but not above, temperatures in the region between 1 and 2 °K. may result in a serious cleanup of helium. It should be possible to avoid this by using enough helium to produce a layer two or three molecules deep if absorption does not occur as well as adsorption. However, the observations indicate that it is advantageous to heat a sample tube to temperatures of 4° or higher for occasional short periods to regenerate the conducting helium.

Summary

The adsorption of helium gas on nickel sulfate heptahydrate has been studied at the temperatures of liquid helium to obtain information relating to thermal equilibrium in calorimeters at these and at lower temperatures.

Equilibrium pressures have been measured for amounts estimated to form surface layers of the order of 1 to 2 molecules deep.

The heat of adsorption at 4.23 °K. was found to be 131, 135, 137 and 148 cal./mole for the equilibrium pressures 1.12×10^{-3}, 7.1×10^{-4}, 5.8×10^{-4} and 1.6×10^{-4} cm., respectively.

When a calorimeter is cooled from 4.23 to 1.35° true adsorption equilibrium is not obtained within the time usually required for various magnetic and calorimetric experiments at these temperatures. In such a case the helium molecules adsorbed at the lower temperature are held more nearly like those of liquid helium.

BERKELEY, CALIF. RECEIVED DECEMBER 9, 1937

[CONTRIBUTION FROM THE CELLULOSE LABORATORY OF BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH]

The Unimolar Tosylation[1] of alpha- and beta-Methyl-*d*-glucosides

BY JACK COMPTON

The unimolar acylation of carbohydrate derivatives containing both primary and secondary hydroxyl groups leads to the preferential esterification of the former.[2] Among the secondary hydroxyl groups that may be present, the one adjacent to the carbonyl group, *i. e.*, position two in the aldose sugars, is usually the more reactive. In certain derivatives, the reactivity of the alpha secondary hydroxyl group is enhanced by the nature of the other substituents to equal that of the primary hydroxyl group. Thus, Lieser and Schweizer[2] found that the partial benzoylation of β-phenyl-*d*-glucoside in pyridine solution led to the formation of 6-benzoyl-β-phenyl-*d*-glucoside in high yield, whereas the partial benzoylation of both α- and β-methyl-*d*-glucoside resulted in the formation of 2,6-dibenzoyl-α-and β-methyl-*d*-glucosides, respectively. On the other hand, the reactivity of the alpha secondary hydroxyl group may be lowered by the nature of the other substituents in the molecule and by the conditions of acylation. Brigl and Mühlschlegel[3] thus have found that the benzoylation of glucose diethyl mercaptal with benzoyl chloride in aqueous alkaline solution led to the formation of 3,4,5,6-tetrabenzoylglucose diethyl mercaptal, but in pyridine solution a mixture of 2,3,4,5,6-pentabenzoylglucose diethyl mercaptal and 3,4,5,6-tetrabenzoylglucose diethyl mercaptal was obtained. The variable reactivity of the alpha secondary hydroxyl group shown in these cases is, perhaps, characteristic of the behavior of the secondary hydroxyl groups in other positions of the sugar molecule.

In the present investigation, a detailed quantitative study has been made of the unimolar tosyla-

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(1) K. Hess and R. Pfleger, *Ann.*, **507**, 48 (1933).

(2) T. Lieser and R. Schweizer, *ibid.*, **519**, 271 (1935).

(3) P. Brigl and H. Mühlschlegel, *Ber.*, **63**, 1551 (1930).