The Adsorption of Helium on Charcoal below 78°K., and Production and Thermometry of Law Temperatures.

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The production of lower temperatures by pumping off the adsorbed gas at a low temperature was first tried by Simon.⑴ Recently Keyes and his coworkers⑵ indicated, in the process of liquefying hydrogen, the practicability of refrigeration at temperatures near 40°K. by desorption of the hydrogen adsorbed at 63°K. The present author intended to obtain various low temperatures between the triple point of hydrogen (14.0°K.) and the boiling point of helium (4.2°K.) without using the helium liquefying apparatus. The desorption of helium is an excellent method for this purpose, but the adsorption of this gas on charcoal at such low temperatures has scarcely been studied.⑶ The author determined the adsorption of helium below 78°K. The temperature below 14°K. was determined with the helium gas thermometer, and the resistance thermometers of constantan and of manganin were calibrated.

Adsorption of Helium. Helium gas used in the adsorption experiment was imported from America and its quality was 95%. The gas used for the gas thermometer was obtained through heating the monazite sand over 750°C., the crude gas was purified through the adsorption on charcoal cooled by liquid nitrogen and by liquid hydrogen respectively. Charcoal at 21°K. adsorbs even the traces of admixed gases together with a small part of helium. The apparatus was very analogous to that of Fig. 1 used in the adsorption experiment.

Experiment on Adsorption. The apparatus is shown in Fig. 1. The activated charcoal is in C. The volume of the gas adsorbed was measured with the burette B. The low temperature was obtained by means of liquid hydrogen or solid hydrogen. The amount of the adsorbent was almost 5 g.

The volume of the helium adsorbed per gram of charcoal at various temperatures and pressures is shown in Table 1. The adsorption isotherms are shown in Fig. 2.

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(1) Simon, *Physik. Z.*, **27** (1926), 790.

(2) Keyes, Gerry, and Hicks, *J. Am. Chem. Soc.*, **59** (1937), 1426.

(3) Dewar, *Ann. chim. phys.*, [8], **3** (1904), 5.

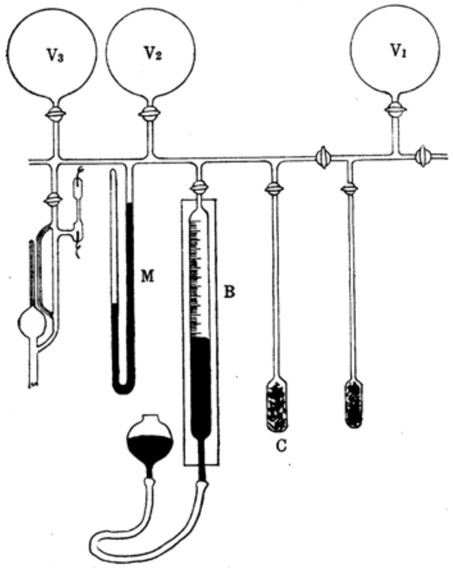

Fig. 1.

Table 1.

Temp. (°K.) \ Press. (cm.)	30	50	76
78.1	4	6	11
53.5	12	15	26
21.3	108	150	180
15.0	192	255	300
12.9	244	310	360

The heat of sorption was determined preliminarily with an evaporation method. It amounts to 1.2 kcal. per mol helium and is much smaller than Dewar's value.(3) The value calculated from the adsorption isotherms according to Clapeyron-Clausius equation deviates largely from the observed value.

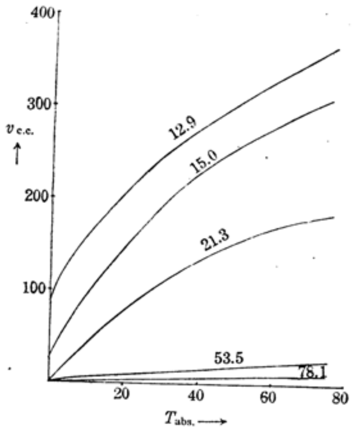

Fig. 2.

Production of Low Temperatures by Desorption. The apparatus was shown in Fig. 3.

Hydrogen or helium gas was introduced into C through V_2, and the charcoal in D was cooled by liquid hydrogen in the vessel B through the gaseous conduction. Helium gas was introduced into D through V_1 and was adsorbed on charcoal isothermally. After the saturation of adsorption was reached the gas for conduction in C was evacuated and the charcoal became adiabatic from the liquid hydrogen.

Adsorbed helium was pumped off as fast as possible. The temperature of the charcoal and the apparatus in D was lowered. In Fig. 3, G shows the bulb of the helium gas thermometer. The lowering of the

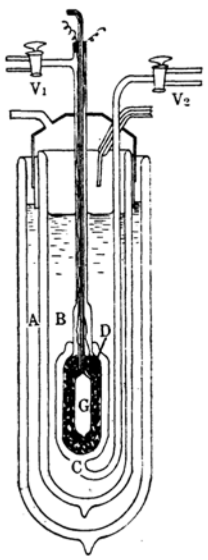

Fig. 3

temperature is dependent on (i) the dimension and adiabatic condition of the apparatus, (ii) the amount of charcoal, (iii) the amount of the adsorbed gas, (iv) the velocity of desorption, and (v) the initial temperature. In practice a large part of the heat of desorption was consumed against the thermal conduction from outward. The lowest temperature obtained in this trial was 5.8°K. To obtain any desired final temperature in certain apparatus containing the fixed amount of charcoal the author controlled the pressure of helium at which the adsorption took place. For example in an apparatus containing 17 g. of charcoal the various final temperatures reached are shown in Table 2. The initial temperature was 14.9°K.

The relation between the final temperature and the pressure at which the adsorption took place was shown in Fig. 4, where the amount of the charcoal was somewhat varied.

Table 2.

Pressure of helium (cm.)	Volume of adsorbed gas (l.)	Final temperature (°K.)
20	2.0	14.4
45	3.6	10.9
59	4.3	9.0
76	5.0	7.2
88	6.1	6.1

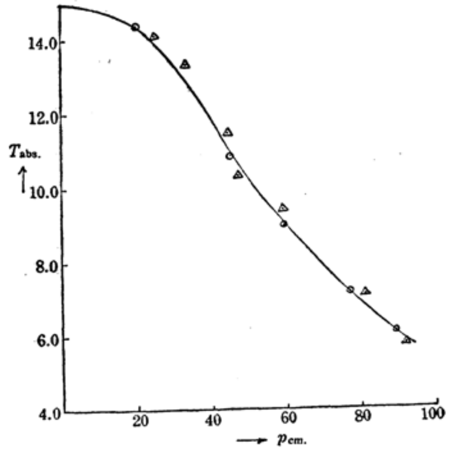

Fig. 4

Helium Gas Thermometer. The construction of the helium thermometer is very analogous to the hydrogen thermometer constructed by the present author,(4) but some modifications have been added. It is shown in Fig. 5. The thermometer bulb is of Pyrex glass and has a cylindrical cavity C in its centre for the resistance thermometer to be calibrated.

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(4) Aoyama and Kanda, this Bulletin, **10** (1935), 472.

A is the adjustor of the mercury level having a thin iron plate and a screw.

The volume of the bulb V is 112.974 c.c. This volume, the capillary of the bulb, and the space of the mercury manometer have to be corrected for the thermal expansion. The linear expansion coefficient of the Pyrex glass is given in Table 3.

The temperature can be determined according to the equation:⁽⁴⁾

$$t = \frac{1}{\beta}\left[\frac{p_t V_0'}{p_0\left\{V_0+\frac{V_s}{1+\beta t_s}\right\}-p_t\frac{V_s'}{1+\beta t_s}}-1\right],$$

where V_s and t_s are the volume and the temperature of the dead space respectively, and p_0 is the pressure of the helium when the bulb is at 0°C. The pressure coefficient β of helium has a value $\beta = 0.00366072$.⁽⁵⁾ To check the accuracy of the gas thermometer measurements the normal boiling point of hydrogen was determined. The vapour pressure tube of hydrogen was inserted into the cavity of the thermometer bulb and the whole was surrounded by liquid hydrogen. The equilibrium pressure in the vapour pressure tube and the temperature of the liquid hydrogen bath were measured (Table 4).

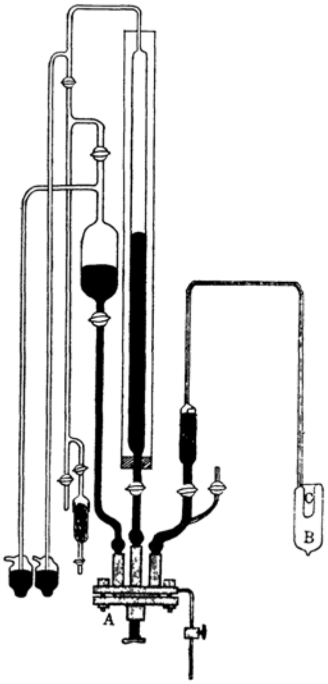

Fig. 5

Table 3.

T(°K.)	273	210	90	21
$\alpha\times10^5$	0.35	0.30	0.10	0.05

Table 4.

p(mm.)	755.10	763.05	768.95	772.05
t(°C.)	−252.75	−252.72	−252.69	−252.68

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(5) Keesom, Van der Horst, and Taconis, *Physica*, **1** (1933), 324.

The normal boiling point becomes −252.73°C. This is in good agreement with the values of other authors: Keesom, Bijl, and Van der Horst⁽⁶⁾ −252.75°; Otto and Heuse⁽⁷⁾ −252.78°; and Southard and Milner⁽⁸⁾ −252.76°.

Calibration of Resistance Thermometer. The resistance thermometer is of a four lead type. The coil was set in the cylindrical cavity of the bulb of the gas thermometer and was buried by the charcoal. The results of calibration are shown in Table 5.

Table 5.

Constantan resistance thermometer.

$R_0 = 49.150$

t (°C.)	R/R_0
−195.72	0.9945
−252.45	0.9728
−256.33	0.9687
−259.65	0.9637
−263.50	0.9544
−265.15	0.9487

Manganin resistance thermometer.

$R_0 = 98.451$

t (°C.)	R/R_0
−194.98	0.9588
−252.66	0.9184
−254.95	0.9168
−257.32	0.9158
−259.81	0.9133
−262.40	0.9113
−264.51	0.9095
−266.59	0.9076
−267.33	0.9067

Both of constantan and manganin have very small temperature coefficients of electric resistance, but their resistances decrease monotonously down to the very low temperature near absolute zero. We can use them as thermometers for extreme low temperatures.

Summary.

The adsorption of helium on charcoal below to 78°K. was measured and the heat of sorption was determined. Systematical trials of the desorption method for the purpose of obtaining low temperatures without liquid helium were described. Resistance thermometers of manganin

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(6) Keesom, Bijl, and Van der Horst, *Proc. Roy. Soc. Amsterdam*, **34** (1931), 78.

(7) Otto and Heuse, *Ann. Physik*, [5], **9** (1931), 486.

(8) Southard and Milner, *J. Am. Chem. Soc.*, **55** (1933), 4378.

and of constantan were calibrated with the helium gas thermometer down to 6°K.

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