EXPERIMENTAL INVESTIGATION OF THE SPECIFIC
HEAT OF POTASSIUM VAPOR

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The specific heat c_p of potassium vapor has been measured by means of a continuous-flow calorimeter in a circulation loop. The results are used to determine the dissociation energy of the K_2 molecule.

Potassium vapor is a mixture of monatomic and diatomic components. At low pressures this vapor may be regarded as a dissociating ideal gas, whose specific heat

$$c_p = \frac{x_1 c_{p_1} + 2x_2 c_{p_2}}{1 + x_2} + \frac{R x_1 x_2}{A(1 + x_2)^3} \left(\frac{\Delta H_D^0}{RT} \right)^2, \tag{1}$$

$$\Delta H_D^0 = \Delta(H^0 - H_0^0) + D_0^0. \tag{2}$$

The first term in (1) is the so-called "frozen specific heat," possessed by a gas mixture in the absence of chemical reactions, including dissociation. The second term is the contribution to the specific heat determined by the dissociation reaction.

It follows from (1) and (2) that the values of the specific heat depend through the quantity ΔH_D^0 on the value of D_0^0 employed in the calculations. However, the dependence of c_p on D_0^0 is further intensified by the fact that the concentrations x_1 and x_2 of the vapor components, calculated from the relation

$$\ln(x_1^2 p/x_2) = \Delta\Phi^*/R - D_0^0/RT, \tag{3}$$

are also very dependent on D_0^0.

Calculations show that at 1100°K and p = 1 bar an increase in D_0^0 by 12% from 0.512 eV to 0.572 eV leads to an increase in the specific heat of the potassium vapor from 0.921 to 1.17 kJ/kg·deg, i.e., by almost 30%.

Thus, the error in c_p is greater than the error in D_0^0 by a factor of 2.5. The quantity D_0^0 also has an important influence on other thermodynamic functions.
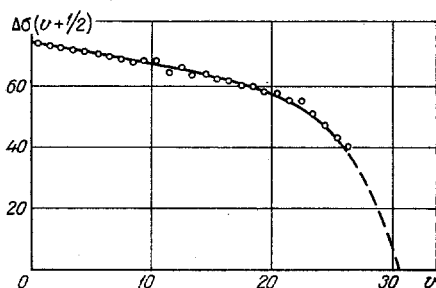

Fig. 1. Graph of the function $\Delta G = f(v + 0.5)$ for the K_2 molecule.

The values of D_0^0 for the K_2 molecule established by different methods [1, 2] are very different; preference is usually given to the value $D_0^0 = 0.51$ eV established spectroscopically [3, 4]. In such investigations the distance ΔG between two neighboring vibration levels of the molecule is established from the wavelength of the spectral lines, this distance is represented graphically as a function of the vibrational quantum number v (Fig. 1), and the value of D_0^0 is computed from the area under the curve. In this case it is very important to use graphs of the function $\Delta G = f[v + (1/2)]$ constructed for both the ground and the excited states of the molecule; the agreement of the results is a criterion of their reliability.
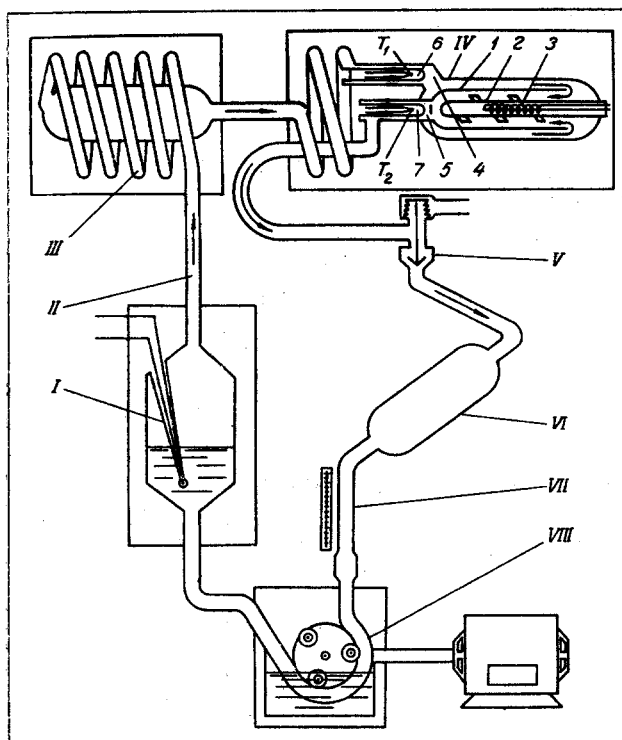
Fig. 2. Diagram of apparatus for measuring the specific heat of potassium vapor.

The wavelength of light can be measured very accurately, but, unfortunately, the spectral lines corresponding to high values of the vibrational number v are not easily differentiable; near $\Delta G = 0$ the graph must be extrapolated, and this introduces a considerable uncertainty into the value of D_0^0. Loomis and Nusbaum [2] distinctly observed, in the spectrum of potassium vapor, bands corresponding to vibrational numbers v' of the excited state of the K_2 molecule up to v' = 20, but they extrapolated the function $\Delta G'$ $= f[v' + (1/2)]$ to zero at v' = 31 taking into account the bands up to v' = 27, which were not reliably observed. However, for the ground state of the K_2 molecule the graph of the function $\Delta G'' = f[v''$ $+ (1/2)]$ was constructed only up to $v'' = 14$ and its extrapolation to zero proved not to be possible at all. Thus, the value $D_0^0 = 0.51$ eV was established in [2] only with respect to the excited state of the K_2 molecule and, moreover, with no great degree of reliability. It differs considerably from the value $D_0^0 = 0.56$ eV established by molecular beam splitting in a magnetic field [1].

In calculating the thermodynamic properties of potassium various investigators use different values of D_0^0 [5, 6], and their results are very different. Accordingly, it was considered important to determine the value of D_0^0 for the K_2 molecule by other methods.

Since in certain regions of pressure and temperature the specific heat c_p is very sensitive to the value of D_0^0, it is desirable, having measured its value experimentally, then to determine D_0^0, using relations (1), (2), and (3). The above example shows that the error in determining the value of D_0^0 may be 2.5 times smaller than the error in measuring c_p. Our measurements of the specific heat of potassium vapor were undertaken with the specific object of improving the accuracy of the value of D_0^0 for the K_2 molecule.

Apparatus. In these experiments we used a continuous-flow calorimeter inserted in a circulation loop (Fig. 2). The potassium vapor formed in the evaporator I, passing through the superheater II and the dryer III, enters the calorimeter IV, where it absorbs a certain amount of heat from the heater. From the calorimeter the vapor passes through the throttle V into the cooler VI, which is bathed in a coolant; the condensate flows into the quartz measuring tube of a flowmeter VII and is then pumped back into the evaporator I by a pump VIII.

All the metal elements of the circulation loop were made of 1Kh18N9T steel. The capacity of the evaporator was 4 liter, a quarter of its volume was occupied by liquid potassium; the temperature at the

TABLE 1. Results of Measurements of the Specific Heat of Potassium Vapor

$T°, K$	p, atm	W, J/h	G, kg/h	$T_1-T_2, °K$	$c_p, \dfrac{\text{kJ}}{\text{kg} \cdot \text{deg}}$	D_0^0, eV
1095	0,94	39,6	0,880	45,0	0,955	0,562
1096	0,94	39,1	0,845	46,0	0,976	0,568
1096	0,91	38,9	0,767	49,5	0,942	0,565
1092	0,87	37,9	0,760	52,0	0,938	0,563
1091	0,87	39,7	0,830	47,0	0,976	0,564
1095	0,90	39,9	0,870	46,0	0,917	0,567
1095	0,88	40,9	0,900	47,0	0,921	0,561
1100	0,95	27,3	0,590	46,0	1,005	0,557
1095	0,94	35,4	0,738	47,7	0,976	0,567

surface of the liquid potassium in the evaporator was measured with a platinum–platinorhodium thermocouple in a stainless-steel sleeve.

The saturated vapor pressure P in the evaporator was determined from the known temperature dependence of the saturation pressure of potassium [7]. In the superheater – a tube 1.5 m long – the vapor was superheated by 50°, in the dryer, flowing between a set of blades, it was freed of residual moisture and at the outlet acquired a temperature equal to the temperature at the calorimeter inlet.

The calorimeter was a cylinder with hemispherical bottoms, a screen 1 separated the space inside the calorimeter into internal and external cavities; the heater 3 was mounted along the calorimeter axis in a sleeve 2 equipped with a set of blades. Vapor passed through the connecting piece 4 into the external cavity of the calorimeter, then, flowing between the heater blades, it was mixed and heated and left at 5. The vapor temperatures at the inlet and outlet of the calorimeter were measured by thermocouples T_1 and T_2 in cavities 6 and 7. The entire calorimeter was placed in a silver vessel, onto which we wound a 600-junction thermocouple to detect the heat flux through the calorimeter walls. Over this thermocouple we slipped a silver jacket onto which we wound a protective heater to compensate the heat flow from the calorimeter. The power of this heater was automatically regulated, so that the thermocouple reading was equal to zero. The heater was covered by a silver shell and a layer of thermal insulation.

The throttle V and the pump VIII serve to separate the region of elevated pressure from the vacuum region of the cooler VI and the flowmeter VII. In view of the lack of low-delivery pumps for pumping liquid metals, we made a special pump VIII in the form of a disk with rollers. When the disk rotated, the roller, rolling along a rubber hose, squeezed out liquid potassium at a temperature ≈100°C.

Throttle V was a valve with the stem connected to a bellows under external helium pressure. When the potassium vapor flowed, it raised the bellows and the stem and opened a path into the cooler; however, if the vapor pressure was lower than the pressure applied to the bellows, there was no flow of potassium vapor.

EXPERIMENTAL AND RESULTS

After carefully pumping out the air from the entire system and heating it to 100°C, we filled the evaporator with potassium in a helium atmosphere. After this we switched on the heaters of the dryer, superheater and throttle and established the experimental temperature in them. At this point the throttle was closed, the heaters of the evaporator and the calorimeter were switched off, the pump was not operating, and the potassium was not circulating in the system. This regime was maintained for several hours, the temperature difference between the inlet and the outlet of the calorimeter being equal to zero. Then the necessary helium pressure was applied to the throttle, heater of the evaporator was switched on, and after the necessary saturated vapor pressure had been created in the latter, the pump was turned on and the potassium began to circulate.

We next turned on both calorimeter heaters and, after establishing a constant temperature difference between the inlet and the outlet, were ready to measure the specific heat. The pump was stopped, a stopwatch started, and condensate began to accumulate in the flowmeter. During this interval, of the order of 6 min, the power of the calorimeter heater, the temperatures T_1 and T_2 at its inlet and outlet, the temperature at the surface of the metal in the evaporator, and the thermocouple reading were continuously monitored. After the flowmeter had filled to a known level, we noted the time, pumped the potassium back from the flowmeter into the evaporator and prepared the system for the next measurement.

The specific heat of the potassium vapor was calculated from the equation

$$c_p = \frac{W}{G(T_1 - T_2)}. \tag{4}$$

In accordance with (1), (2), and (3), the specific heat c_p is a function of pressure and temperature. The reference temperature T was taken equal to the mean temperature in the calorimeter, $T = (T_1 + T_2)/2$, the reference pressure was taken equal to the pressure in the evaporator, since by means of a special experiment it was established that the hydrodynamic resistance to the vapor on the path from the evaporator I to the calorimeter IV was negligibly small. The results of the experiments are presented in Table 1.

The error in measuring the specific heat is composed of the error in measuring the quantities entering into the right side of (4) and the reference errors associated with the errors in measuring the temperature T and the pressure P. An analysis showed that the maximum error in measuring the specific heat is 3%.

At a pressure of up to 1 atm potassium vapor, as shown in [8], may be regarded as a dissociating ideal gas, to which relations (1), (2), and (3) apply. These equations were solved graphically, and for each of the experimental values of c_p we calculated the corresponding value of D_0^0; these are presented in the table. As stated above, the error in determining D_0^0 is approximately 2.5 times smaller than the error in measuring c_p and is approximately 1.3%. Thus, from the experiments described we obtain for the K_2 molecule an average value of $D_0^0 = 54,400 \pm 700$ J/mole (0.564 ± 0.008 eV).

Within its margin of error this result is in agreement with the value $D_0^0 = 53,750$ J/mole obtained from experiments on the saturation pressure of potassium [8]. All this confirms the value $D_0^0 = 0.56 \pm 0.04$ eV obtained for the K_2 molecule by the beam splitting method [7]. At the same time, it does not confirm the value $D_0^0 = 0.51 \pm 0.02$ obtained by the spectroscopic method and recommended in [3, 4].

NOTATION

x_1, x_2	is the mole concentrations of vapor components;
c_p, c_{p_1}, c_{p_2}	are the specific heat of vapor and its components, J/kg·deg;
ΔH_D^0	is the energy of dissociation reaction, J/kg;
T	is the absolute temperature, °K;
A = 39.10	is the atomic weight of potassium;
$H^0 - H_0^0$	is the enthalpy difference, J/kg;
D_0^0	is the dissociation energy of the potassium molecule;
P	is the vapor pressure, atm;
$\Delta\Phi^*$	is the variation of standard thermodynamic potential in the dissociation process, J/kg·mole·deg;
v	is the vibrational quantum number;
ΔG	is the difference of energy levels, cm^{-1};
W	is the power of calorimeter heater, J/h;
G	is the flow rate of liquid metal, kg/h;

R = 8314 J/kg·mole·deg.

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