

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

THE VAPOR PRESSURE AND VAPOR DENSITY OF SODIUM

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Some years ago Rodebush and DeVries¹ published the results of measurements of the vapor pressure of sodium at very low pressures by the effusion method of Knudsen. In this paper they reviewed previous work. The only previous measurements that appeared good were those of Haber and Zisch² in the pressure range 2–12 mm. Their measurements were made by a dynamic method. Edmondson and Egerton³ have repeated and confirmed the work of Rodebush and DeVries. No satisfactory measurements are to be found in the literature for higher pressures except some not very recent determinations of the boiling points.⁴ It seems doubtful whether a boiling point can be determined at high temperatures with a satisfactory degree of accuracy.

There is plenty of evidence in the literature that the vapor of sodium is monatomic. Robitsch⁵ determined the velocity of sound in the vapor at the boiling point and calculated the ratio of specific heats to be 1.68. Taylor⁶ found no evidence of molecules in the saturated vapor at pressures of 10^{-2} mm. When the vapor pressure data of Rodebush and DeVries, Edmondson and Egerton and Haber and Zisch are plotted together with the boiling points as found in the literature on a $\log p-1/T$ diagram, the points all fall very close to a straight line. Since these vapor pressures obtained by both the effusion and the dynamic methods involve the assumption of normal vapor density,⁷ the excellent agreement of the results by the different methods seems to argue for a normal vapor density. Rodebush⁸ used these data to calculate the entropy of the sodium atom in the vapor state and obtained excellent agreement with the theory for an atom in a 2S ground state.

However, the straight line obtained in the vapor pressure plot previously mentioned does not agree with the value of C_p of $5/2R$ to be expected for a monatomic vapor. With the discovery of a band spectrum due to diatomic molecules in the vapors of the alkali metals, it was established that these vapors could not longer be considered strictly monatomic.

¹ Rodebush and DeVries, *THIS JOURNAL*, **47**, 2488 (1925).

² Haber and Zisch, *Z. Physik*, **9**, 325 (1922).

³ Edmondson and Egerton, *Proc. Roy. Soc. (London)*, **A113**, 520 (1927).

⁴ Heycock and Lamplough, *Proc. Chem. Soc.*, **28**, 3 (1912).

⁵ Robitsch, *Ann. Physik*, **38**, 1027 (1912).

⁶ Taylor, *Phys. Rev.*, **28**, 576 (1926).

⁷ The pressure calculated by the dynamic method varies inversely as the assumed vapor density, while for the effusion method the relation is more involved.

⁸ Rodebush, *Proc. Nat. Acad. Sci.*, **13**, 185 (1927).

In the case of potassium, Carelli and Pringsheim⁹ showed that the association was small, but in the case of sodium Loomis¹⁰ calculated the heat of dissociation to be 1.0 ± 0.1 volt and thermodynamic calculations¹¹ have been made which predict that there will be more molecules than atoms in sodium vapor at the boiling point. In view of the conflicting evidence it seemed desirable to determine accurately the amount of association in saturated sodium vapor.

Method

Since the only material suitable as a container for sodium at high temperatures is pure nickel, it was impossible to use the ordinary methods of measuring vapor pressure. The method used involves a simple application of Dalton's law of partial pressures. The sodium was vaporized in a large container in the presence of argon. The container was connected by a narrow tube to a mercury manometer. The sodium vapor which diffused up the tube was condensed and refluxed back into the container. When a static condition was established, the external pressure of argon was equal to the combined pressure of sodium and argon in the container. From the known volumes and the quantity of argon in the apparatus the pressure of the sodium can be calculated.

The vapor density was measured by determining the amount of sodium vaporized when a measured quantity of argon was passed over metallic sodium.

Apparatus

A. Vapor Pressures.—In general the vapor pressure apparatus consisted of a mercury manometer connected to a nickel bomb in which the sodium was heated. A diagram of the nickel bomb is given in Fig. 1. The bomb was constructed by welding a nickel tube about 30 cm. long and 0.5 cm. in internal diameter to a cylindrical nickel container 10 cm. high and having a 7-cm. base. In order that sodium vapor would not distil into the manometer system, a cylindrical copper water jacket 7 cm. long was soldered to the nickel tube 8 cm. above the top of the nickel container. This copper jacket, filled with boiling water in order to prevent the solidification of the sodium, served as a condenser to reflux the sodium back into the bomb. The nickel tube and

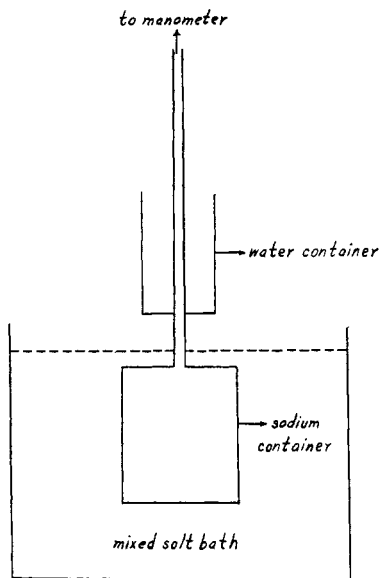


Fig. 1.

⁹ Carelli and Pringsheim, *Z. Physik*, **44**, 643 (1927).

¹⁰ Loomis, *Phys. Rev.*, **31**, 323 (1928).

¹¹ Harrison and Slater, *ibid.*, **26**, 176 (1925); Villars, *Proc. Nat. Acad. Sci.*, **14**, 508 (1928).

pyrex manometer were connected by means of a picein seal. A water-jacketed condenser placed between the picein seal and the copper jacket prevented the picein from melting.

Two stopcocks were sealed into the arm of the manometer connected to the nickel bomb, in order that the system might be evacuated and argon admitted. The argon was passed from a gas measuring buret through a constricted capillary which permitted as small amounts of argon as desired to be admitted into the system.

By the use of a leveling bulb, the mercury in the arm of the manometer connected to the nickel bomb was maintained at a constant level in order that the volume above this level would remain constant. The other arm of the manometer was evacuated with a Cenco Hyvac pump in order to make the manometer of the absolute type.

The bomb was immersed in a mixed salt bath of equal parts by weight of sodium chloride and potassium carbonate (m. p. 560°), which was held in an electric furnace with a cylindrical iron core. A uniform temperature was maintained throughout the bath by means of a mechanical stirrer. Temperature control was obtained by varying the 220-volt alternating current through the furnace by means of a hand-controlled rheostat. All temperatures were measured with a platinum-platinum-rhodium thermocouple. The thermocouple, which was sheathed in quartz, was protected from the corrosive action of the salt bath by means of a close fitting iron tube, placed directly next to the bomb.

B. Vapor Densities.—Vapor densities were determined by a dynamic method, employing the apparatus shown in Fig. 2.

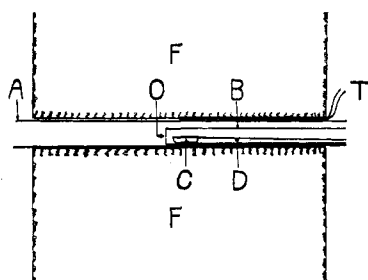


Fig. 2.

F is an electric furnace with a cylindrical copper core. A and B are nickel tubes. One end of B was constricted to a small orifice O about 1.5 mm. in diameter. The other end of B was connected to a drying train consisting of a sulfuric acid bubbler, soda and lime, and phosphorus pentoxide drying tubes, through which argon was admitted from a cylinder. D is a nickel wire for inserting the nickel boat C into Tube B. The outlet of Tube A leads to a five-liter aspirator bottle containing water saturated with argon at atmospheric pressure. The rate of flow of the argon was regulated by the rate of removal of water from the aspirator bottle and the volume

of argon passed was determined by measuring the volume of water removed. The system was connected to the atmosphere through a sulfuric acid bubbler and the pressure of argon was kept equal to that of the atmosphere by regulation of the automatic valve on the argon cylinder. The thermocouple is shown at T.

Method

A. Vapor Pressure.—The nickel bomb was first evacuated by means of a Cenco Hyvac pump and filled with argon. About 6 g. of sodium which had been put through a sodium press was inserted into the bomb, and the nickel tube sealed to the manometer. The system was evacuated for several hours at a temperature of 400 to 500° in order to remove all volatile impurities from the sodium. After this treatment, a measured amount of argon was admitted into the system through the capillary tube and the temperature of the bath regulated by means of a rheostat until a constant temperature had been maintained for thirty minutes or more. The temperatures of the bath, the cooling water and the room, and the total pressure in the system as indicated by the manometer, were recorded. The pressure readings of the manometer were read to 0.1 mm. by means of a cathetometer. The temperature of the bath was then raised to the next desired

temperature and the readings recorded as before. This procedure was repeated until the vapor pressures of sodium up to the boiling point had been determined, argon being admitted into the system from time to time in order to keep the total pressure to approximately twice the vapor pressure of the sodium.

The vapor pressure of the sodium was calculated from the equation

$$P_{\text{Na}} = P_{\text{T}} + \frac{P_{\text{T}} \left(\frac{V_2}{T_2} + \frac{V_3}{T_3} + \frac{V_4}{T_4} \right) - \frac{P_{\text{A}} V_{\text{A}}}{T_{\text{A}}}}{V_1/T_1} \quad (1)$$

In this formula P_{Na} is the vapor pressure of the sodium, P_{T} is the total pressure of the system as indicated by the manometer, V_2/T_2 , V_3/T_3 and V_4/T_4 are the various volumes of the apparatus external to the bath divided by their corresponding temperatures, V_1 is the volume occupied by the sodium vapor at the temperature T_1 , and P_{A} , V_{A} and T_{A} are the pressure, volume and temperature of the argon when admitted into the system.

This equation was derived from a simple consideration of the perfect gas law. If M_{A} moles of a gas are in an enclosed system whose total volume is divided into the several volumes V_1, V_2, \dots, V_n , which are subjected to the corresponding temperatures $T_1, T_2, T_3 \dots T_n$, then

$$M_{\text{A}} = \frac{P_{\text{T}}}{R} \left[\frac{V_1}{T_1} + \frac{V_2}{T_2} + \dots + \frac{V_n}{T_n} \right] \quad (2)$$

where P_{T} is the total pressure of the gas and R the gas constant. If V_1 be occupied by not only gas A but gas Na whose pressure is P_{Na} , then

$$M_{\text{A}} = \frac{(P_{\text{T}} - P_{\text{Na}})}{R} \frac{V_1}{T_1} + \frac{P_{\text{T}}}{R} \left[\frac{V_2}{T_2} + \dots + \frac{V_n}{T_n} \right] \quad (3)$$

If M were measured at a pressure P_{A} , V_{A} and T_{A} , then

$$M_{\text{A}} = \frac{P_{\text{A}} V_{\text{A}}}{RT_{\text{A}}} \quad (4)$$

Substituting this value for M_{A} in Formula 3 and multiplying through by R , the gas constant, Equation 5

$$\frac{P_{\text{A}} V_{\text{A}}}{T_{\text{A}}} = (P_{\text{T}} - P_{\text{Na}}) \frac{V_1}{T_1} + P_{\text{T}} \left(\frac{V_2}{T_2} \dots + \frac{V_n}{T_n} \right) \quad (5)$$

is obtained, which when divided by V_1/T_1 and the terms rearranged, gives Equation 1. The volumes were determined by weighing the apparatus first empty and then filled with water, the difference in weight divided by the density of water at the temperature of the water, giving the volume. The total volume of the system was also checked in another manner. A bulb was blown in the manometer system and marks made above and below the bulb in such a manner as to make the capacity of the bulb exactly 55 cc. The system was then evacuated by means of a Cenco Hyvac pump and refilled with argon. With the system at atmospheric pressure, P_1 , the mercury level in the manometer was then adjusted to the mark above the bulb. All stopcocks were then closed and the mer-

cury level in the manometer adjusted to the mark below the bulb. When temperature equilibrium was obtained, the new pressure reading P_2 was observed, and the total volume of the apparatus, V_1 , calculated from the equation, $P_1V_1 = P_2(V_1-55)$. The volume of the bomb as obtained in this manner checked within a few tenths of a per cent. with the volume as obtained by weighing the bomb empty and filled with water. A final check on all volumes was also made when dismantling the apparatus; again the results were in good agreement with the volumes as determined above. At high temperatures allowance was made for the change in volume due to the expansion of the nickel bomb and the decreased density of sodium.¹²

The supply of dried argon was kept in a gas buret over mercury. The buret containing the argon was graduated to 0.05 cc. and estimation could be made to 0.01 cc. As no less than 10 cc. of argon was admitted into the system at one time, the error from this source should not exceed a few tenths of a per cent. The capacity of the buret was carefully checked in order that no volume error should enter from this source. Manometer readings were made with a cathetometer having an invar scale and were reproducible to 0.1 mm.

It is true that in deriving Equation 1 from which the vapor pressures were calculated, the assumption was made that the temperature boundaries, *i. e.*, T_1 , T_2 , etc., were sharp and well defined. This assumption was justified, as the external volume, *i. e.*, the volume not actually contained in the bath, was very small (less than 10%) compared to the total volume of the system. Hence, the error due to the temperature gradients is of little consequence.

B. Vapor Densities.—In making a vapor density determination, the entire vapor density apparatus was first filled with argon. The furnace was brought up to the proper temperature, and 1 to 2 g. of sodium, which had been previously put through the sodium press, was placed in the boat C and introduced into the tube B. Argon at a constant rate of flow was passed through tube B over boat C containing the sodium at the desired temperature. Saturated with sodium vapor, the argon passed through the small orifice O, and deposited the sodium in the cooler portion of the tubes A and B. A steady rate of flow of argon was maintained until from 2 to 2.5 liters had passed over in this manner. The moles of argon passed were calculated from the volume of water, after correcting for the vapor pressure of the water. At the end of the run the flow of argon was cut off, the furnace shut down, the boat removed from tube B and tubes A and B withdrawn. The amount of sodium which had deposited upon tubes A and B was determined by titration with 0.1 or 0.5 *N* hydrochloric acid solution as seemed best.

¹² "International Critical Tables."

The vapor density of the sodium was calculated from the following equation

$$M_{\text{Na}} = \frac{P_{\text{T}} W_{\text{Na}}}{P_{\text{Na}} N_{\text{A}}} - \frac{W_{\text{Na}}}{N_{\text{A}}} \quad (6)$$

W_{Na} is the weight in grams of the sodium which saturated N_{A} moles of argon, P_{T} is the total pressure of the system, P_{Na} is the vapor pressure of the sodium at the temperature at which the vapor density run was carried out, and M_{Na} the molecular weight of the sodium. If gas Na and A occupy a system at a total pressure of P_{T} , the partial pressure of gas Na, P_{Na} , is equal to the total pressure times its mole fraction in the mixture or

$$P_{\text{Na}} = P_{\text{T}} \frac{\frac{W_{\text{Na}}}{M_{\text{Na}}}}{\frac{W_{\text{Na}}}{M_{\text{Na}}} + N_{\text{A}}} \quad (7)$$

Upon simplification of this equation, Equation 6 is obtained.

A. Materials, Analytical Methods, Etc.—In this work a commercial grade of sodium was used. Spectroscopic tests made on the sodium showed it to be free from lithium and potassium. The hydrochloric acid was standardized with a standard solution of sodium hydroxide. The sodium hydroxide was standardized with potassium acid phthalate, which was kindly furnished by Dr. L. W. Elder of this Laboratory. The normalities of the acid solutions were checked with sodium carbonate solutions. Methyl orange was used as an indicator in titrating the sodium. The argon was furnished by the Cleveland Wire Works, Cleveland, Ohio, and from their analysis was 99.7% pure, the remaining 0.3% being chiefly nitrogen. No oxygen and only traces of carbon dioxide were present in the argon.

The platinum-platinum-rhodium thermocouple was calibrated frequently against fixed thermometry points. The latest directions of the Bureau of Standards were very closely followed in the calibration.¹³ The freezing points of silver, copper-silver eutectic, and aluminum, and the boiling point of sulfur were taken as the fixed standard points. The silver was of very high purity (99.99%), while the copper and aluminum were Bureau of Standards samples. All of the freezing points were sharp and well defined.

Results

Vapor Pressure.—The vapor pressure data are given in Table I. A preliminary plot on a $\log -1/T$ diagram of these results together with the results of Rodebush and DeVries and Edmondson and Egerton at low pressures indicated that the data over the whole range of pressures could

¹³ Roeser, *Bur. Standards Jour. of Research*, 3, 343 (1929).

TABLE I
VAPOR PRESSURES
Run 1

Temp. of sodium, °K.	Argon			Total pressure	Vapor pressure of sodium
	Vol., cc.	Temp., °K.	Pressure, mm.		
924.1	9.58	300.4	743.9	97.2	48.82
939.8				105.6	58.40
950.5				109.9	63.19
973.7	7.73	301.1	744.2	185.6	96.12
989.4				202.5	115.9
999.3				214.2	129.7
1020.1	12.22	300.8	744.1	318.6	158.9
1044.5				365.1	214.2
1063.3				412.8	272.0
1082.9				476.4	350.8
1117.9				581.2	481.5

$V_1 = 306.8$ cc.; $V_2 = 3.32$ cc.; $T_2 = 373$ °K.; $V_3 = 5.34$ cc.; $T_3 = 294.2$ °K.; $V_4 = 15.50$ cc.; $T_4 = 300.0$.

Run 2

938.8	11.35	298	746	123.1	65.88
946.9				125.6	68.58
969.5				146.5	93.70
999.5	9.50	298.1	746.4	245.7	139.1
1033				305.5	211.2
1049.9	8.18	298	746.2	395.5	254.0
1070.4				448.5	312.4
1089.3				496.7	378.4
1113.1				479.5	482.5

V_1, V_2, V_3 and V_4 same as in Run 1; $T_2 = 373$ °, $T_3 = 293.7$ °, $T_4 = 296.2$ °.

Run 3

936.7	10.02	297.6	747.8	116.0	67.37
953.2				121.6	73.55
978.7	10.1	297	749.1	216.5	110.1
1011.9				263.3	165.5
1040.7				314.7	228.1

Volumes same as above; $T_2 = 373$ °; $T_3 = 292.4$ °; $T_4 = 294.7$ °.

be satisfactorily represented by a straight line. By the method of least squares a simple equation

$$\log p_{\text{mm}} = A - \frac{B}{T} \quad (8)$$

was obtained with values for the constants

$$A = 7.5165 \pm 0.0075.$$

$$B = 5383.0 \pm 5.7$$

This gives a satisfactory value for the probable error (2-3%) but the deviations of individual measurements are large. It is difficult to see how high results would be given by the experimental method, while low results might be explained by failure to obtain saturation with sodium vapor in the vapor space within the bomb although ample time for equilibrium to be

established was always allowed. Furthermore, the results of the first run are all below the values given by Equation 8. If we reject the first run as being for some unknown reason unsatisfactory, and consider only the last two runs, we obtain a set of readings which are on the average several per cent. higher and much more consistent. The equation

$$\log p_{mm} = 7.5510 - \frac{5400.0}{T} \tag{9}$$

fits the low pressure data almost as well as Equation 8 and with the exception of one or two points at intermediate pressures, where larger errors

TABLE II
DATA

Data of Rodebush and DeVries and of Edmondson and Egerton			Data of Rodebush and Walters		
Temp., °K.	Pressure, mm.			Calcd. × 1	Obs. × 1
	Calcd. × 10 ³	Obs. × 10 ³			
454.9	0.0480	0.04929	938	63.3	65.88
473.4	.138	.1412	946.9	70.1	68.58
492.9	.390	.3880	969.5	96.8	93.70
495.9	.469	.4575	999.5	141.6	139.1
513.0	1.07	1.030	1033	210	211.2
514.3	1.42	1.140	1049.9	267	254.0
534.3	2.89	2.852	1070.4	319	312.0
544.4	4.28	4.163	1113.1	392	378.4
570.7	12.50	12.31	1089.3	500	482.5
			936.7	61.1	67.37
			953.2	76.9	73.55
			978.7	107.4	110.1
			1011.9	166.4	165.5
			1040.7	229	228.1

are to be expected, fits the high pressure data very well, as is shown in Table II and Fig. 3. The two equations are essentially coincident at low

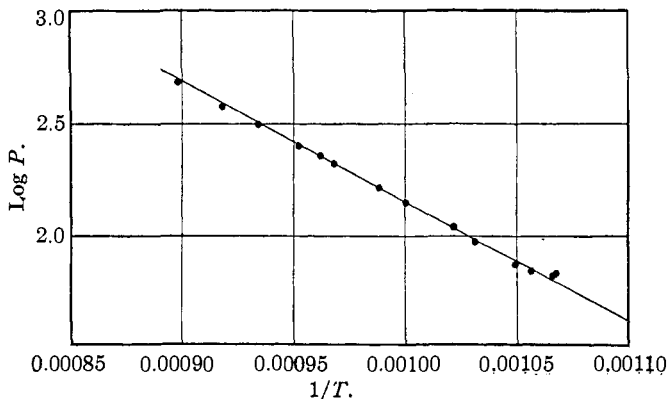


Fig. 3.

pressures but give values for the boiling point of sodium which differ by 6°. Equation 8 gives a value for the boiling point that is in agreement with the figures given in the literature but these figures might easily be in error by 5–10°.

Vapor Density.—Vapor density results are given in Table III. Measurements were made at two different temperatures, 705.8 and 570.5°. The effect of rate of flow on the amount of sodium deposited was studied and it was found that fairly consistent results could be obtained when the rate was between 10 and 25 cc. per minute. A blank run with no gas flowing at 705.8° showed that 0.04–0.05 g. of sodium would diffuse into the outer tube in three hours. The apparent molecular weights in Table III

TABLE III
VAPOR DENSITY DATA

No.	Rate of flow, cc. per min.	Vol. argon, liters	Temp. of argon, °C.	Barometer, mm.	Sodium, g.	Mol. wt.
Temperature of sodium, 705.8°						
31	22.2	2.0	24.2	739.1	0.3055	24.2
32	25.6	2.0	23.5	745.5	.3077	24.3
33	25.0	2.0	24.3	745.9	.3208	25.4
34	22.4	2.0	24.0	753.0	.3089	24.5
35	16.1	2.5	22.9	740.9	.4078	25.7
36	15.3	2.5	21.3	740.9	.3920	24.5
37	10.5	2.0	23.3	740.6	.3190	25.2
38	25.9	2.0	20.0	746.8	.3156	24.6
39	15.6	2.0	23.6	746.5	.3202	25.2
40	27.4	2.0	20.3	749.8	.3064	23.8
41	23.3	2.0	23.3	741.6	.3144	24.7
42	20.0	2.0	22.0	742.3	.3128	24.5
43	29.9	2.0	25.0	746.5	.3001	23.9
44	15.7	2.0	25.2	746.4	.3089	24.7
45	35.1	2.0	27.4	745.0	.2696	23.3
46	9.2	2.0	26.8	744.5	.3199	25.7
Temperature of sodium, 570.5°						
47	18.4	2.5	22.8	746.5	0.0472	26.1
48	16.4	2.5	22.1	743.7	.0458	25.3
49	17.4	2.5	23.2	741.0	.0435	24.0
50	18.1	2.5	22.0	745.7	.0449	24.7
51	19.2	2.5	22.0	744.9	.0490	26.9
52	19.1	2.5	23.6	739.2	.0485	26.9
53	19.7	2.5	25.7	734.9	.0474	26.6
54	11.6	2.5	21.4	735.6	.0508	27.9

Argon collected over water at same temperature as the gas.

have been calculated using Equation 8. A markedly different result is obtained using Equation 9 and the average values for apparent molecular weights (omitting runs where the rate of flow was too fast) are tabulated below.

TABLE IV

Temp., °C.	Equation 8		Equation 9	
	Pressure, mm.	Mol. wt.	Pressure, mm.	Mol. wt.
705.8	104.2	25.0	108.2	24.1
570.5	13.5	26.0	14.0	25.1

These results on vapor density will be discussed in a later paragraph.

Errors.—The constant errors in the vapor pressure measurements should not be greater than the calculated probable error. The uncertainty in the temperature measurements is very small since the fused salt bath was very easily controlled and the thermocouple was carefully calibrated. The pressures given are in mm. of mercury at room temperature since the accuracy does not justify calculation to 0°. The estimation of the external volumes of the apparatus corresponding to different zones of temperature involves an uncertainty which has been estimated to give a probable error of 0.5%. In the vapor density determinations the probable errors in the determination of gas volumes and amounts of sodium vaporized were certainly less than 1%. The temperature control was more uncertain in the furnace than in a fused bath but the temperature was held constant to 0.5° and explorations with the thermocouple indicated that a zone of nearly constant temperature extended for a considerable distance in either direction from the point where the sodium was vaporized.

The Dissociation Equilibrium in Sodium Vapor.—There appears to the authors to be no question of the existence of an appreciable amount of Na₂ molecules in sodium vapor. Postponing for the moment the incontrovertible evidence of band spectra, we believe the vapor pressure curve by itself is evidence for the existence of molecules. The vapor pressure data are of sufficient accuracy to show that a straight line is obtainable on the $\log p-1/T$ plot and this straight line indicates some abnormality of vapor density, as has been stated before. At the low pressures involved, the natural assumption to make is that the abnormal vapor density is due to the presence of molecules.

The results of Table IV, no matter which equation is preferred, are impossible to explain, however, because they indicate that the apparent molecular weight of the saturated vapor decreases with increasing temperature. This could only be true if the heat of dissociation were greater than the apparent molal heat of vaporization, but if that were true it can readily be calculated that the apparent molecular weight of sodium would be far greater than the observed values in Table IV. The authors are, therefore, inclined to reject the results for vapor density at the higher pressure and temperature for the same reason that they are inclined to reject low values for vapor pressure. It seems probable that saturation could not be obtained, perhaps because of rapid diffusion of the vapor to

the cooler portion of the tube. This difficulty would not be remedied by reducing the rate of flow of the inert gas. On the other hand, the authors now believe the results obtained at 570.5° to be reliable, although the results are higher than those obtained by Haber and Zisch with the same method in the same temperature range. We have supposed the experimental errors to be greater because of the smaller amounts of sodium transferred but these difficulties are trivial compared to the difficulty of saturating the inert gas. The results at the lower temperature appear on the whole the more consistent. Accordingly we believe Equation 9 to represent the vapor pressure of sodium with satisfactory accuracy and the vapor density as obtained with this equation at 570.5° to be substantially correct.¹⁴ Gibson and Heitler¹⁵ have derived an equation relating the dissociation constant of a diatomic gas to the heat of dissociation, and certain constants calculated from spectroscopic data. Their equation may be written

$$\log K = -\frac{\Delta H_0}{4.575T} + \frac{3}{2} \log \left(\frac{\pi m k T}{h^2} \right) - \log \frac{8\pi^2 I}{h^2} + \frac{\log(1 - e^{-h\nu/kT})}{\log 2 + \log(2j + 1)} \quad (10)$$

Here K is the constant of Equation 10 above expressed in c. g. s. units, ΔH_0 is the heat of dissociation at absolute zero, h is Planck's constant, I is the moment of inertia of the Na_2 molecule or 179.5×10^{-40} g. cm.², ν is the vibrational frequency of the Na_2 molecule or 158.5 cm.⁻¹ and j is the angular momentum of the sodium atom, which is $1/2$, since its ground state is ^2S . The sodium atom has a nuclear spin of several half units, and a term $2 \log(2s + 1)$ should be introduced into the equation were it not for the fact that there are two kinds of sodium molecules similar to ortho and para hydrogen. There are $(s + 1)(2s + 1)$ possible spin eigen-functions that are symmetric in the nuclei and $s(2s + 1)$ that are antisymmetric in the nuclei. This gives a total multiplicity of $(2s + 1)^2$ for the rotational levels, which just cancels the term $2 \log(2s + 1)$ for the atoms.

The only uncertainty involved in the calculation of the constant for the dissociation equilibrium by Equation 11 is the value to be used for the heat of dissociation of the Na_2 molecule. The value calculated by Loomis is 1.0 ± 0.1 volt and Kinsey¹⁶ has estimated that it may be as low as 0.84 volt = $19,360$ cal. It does not seem probable that it can be much less than this. Using this figure we calculate K for the equilibrium $\text{Na}_2 \rightleftharpoons 2\text{Na}$ to be 10^5 (pressure in c. g. s. units) at 570.5° and the ap-

¹⁴ Our confidence in these results is greatly strengthened by the receipt of a private communication from R. Ladenburg in which he informs us that he has repeated the work of Haber and Zisch at the Kaiser Wilhelm Institute with great care and has obtained results that are in substantial agreement with ours.

¹⁵ Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

¹⁶ Kinsey, *Proc. Nat. Acad. Sci.*, **15**, 37 (1929).

parent molecular weight to be 26.0. This is perhaps as good agreement as one can hope for. An apparent molecular weight of 27 is predicted for sodium vapor at 705.8° and this value cannot be reconciled with the values given in Table IV.

The Entropy of Sodium Vapor.—Rodebush¹⁷ calculated the entropy of sodium vapor and showed it to be in close agreement with the theoretical value predicted for an atom in ²S state. This calculation is confirmed by our new measurements since the saturated vapor is shown to be largely monatomic at lower temperatures and the vapor pressure measurements of Rodebush and DeVries are confirmed. Theoretically the entropy should be greater than that calculated by an amount $R \ln (2s + 1)$, and if the heat capacity of metallic sodium were measured to a sufficiently low temperature, a heat effect would doubtless be found corresponding to the change in orientation of the nuclear spin.^{17,18} This heat effect is so small and at so low a temperature that it is not likely to be observed, although the corresponding entropy change is not negligible.

Summary

The vapor pressure of sodium has been measured over the temperature range from 650–850°.

The preferred vapor pressure equation is

$$\log p_{\text{mm.}} = 7.5510 - \frac{5400.0}{T}$$

The equation gives good agreement with previous data down to pressures of 10^{-4} mm.

The apparent molecular weight of saturated sodium vapor has been determined at 570.5 and 705.8°. The values at the lower temperature are believed to be more nearly accurate and are in fair agreement with the value calculated from spectroscopic data.

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¹⁷ Rodebush, *ibid.*, 13, 185 (1927).

¹⁸ *Phys. Rev.*, 35, 210 (1930).