tion with electrolytic processes of all kinds. Under conditions where the potentials to be measured are temporary or unsteady in nature this apparatus will be found particularly useful because of its continuous and direct-reading features.

Summary

A device is described which, by making use of the three-electrode vacuum tube as a voltmeter, and as a direct current amplifier, serves to indicate upon the scale of a milliammeter the potential between any two electrodes ordinarily used in electrochemical work. This device does not draw an appreciable current from the source to be measured, and is continuous and automatic in its operation. It is particularly adapted to use in electrotitration.

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

THE VAPOR PRESSURE OF SODIUM

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While it is probably true that the vapor-pressure equation for a metal can be set up from a single measurement (for example, of the boiling point) and the quantum theory of monatomic gases,[1,2,3,4] the extrapolation necessary is likely to involve considerable error. The validity of the simple equation for the entropy of monatomic gases has even been questioned by Simon[5] and while the authors believe Simon to be in error, actual measurements of vapor pressure are far more satisfactory than hypothetical calculations.

In the case of sodium, existing data are especially unsatisfactory. Gebhardt[6] determined the vapor pressure of sodium by the boiling-point method, but his results do not agree with those of Haber and Zisch[7] determined by a dynamic method. Gebhardt's values are for temperatures 40–50° lower than those given by Haber and Zisch, who determined only four pressures between 470° and 570°. Hackspill[8] determined four irregular points between 350° and 400° by a method that can be questioned.

[1] Tetrode, *Ann. Physik*, **38**, 434 (1912).

[2] Einstein, *Ber. Berl. Akad.*, **261** (1924).

[3] Millar, THIS JOURNAL, **45**, 2323 (1923).

[4] Egerton, *J. Chem. Soc.*, **123**, 3204 (1923).

[5] Simon, *Z. physik. Chem.*, **110**, 572 (1924).

[6] Gebhardt, *Dissertation*, Erlangen, **1903**. His data are also published in the article by Kroner, *Ann. Physik*, **40**, 483 (1913).

[7] Haber and Zisch, *Z. Physik*, **9**, 325 (1922).

[8] Hackspill, *Compt. rend.*, **154**, 877 (1912).

The boiling point of sodium was determined by Gebhardt, but the values accepted in this paper are those found by Heycock and Lamplough.[9]

Knudsen's method was used for determining the vapor pressures in the range from 10^{-5} to 10^{-3} mm. of mercury. This method is based on the flow of a gas through an opening whose diameter is small as compared with the mean free path of the molecule and whose edges must be sharp. The vapor pressure is calculated from the amount of vapor passing through the opening in a definite period of time at a constant temperature. The theory of the method may be developed as follows. The number of molecules falling on a unit area in unit time is $^1/_4 nv$, where n is the number of molecules per unit volume and v is the average velocity per molecule. The mass falling upon an area a in t seconds is given by $m = {}^1/_4\, \rho v a t$. From the kinetic theory of gases, $RT = M\mu^2/3$; $pM = \rho RT$ and $v = \sqrt{(8/3\pi)}\mu$, where μ is the root-mean-square-velocity, v is the average velocity, ρ is the density per cc., M is the molecular weight, and the other symbols have their usual significance. Making these substitutions, we have the formula which is used for the calculation of the vapor pressure,[10] $m = p.a.t.\sqrt{m/(2\pi RT)}$.

This formula was first applied by Knudsen[11] to determine the vapor pressure of mercury between —10° and 25°. Since then Egerton has determined the vapor pressures of zinc, cadmium, mercury[12] and lead[13] by the same method with only slight experimental modifications.

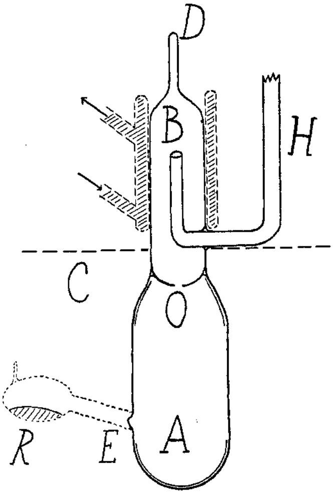

Fig. 1.

Experimental Part

The apparatus (see Fig. 1) was made entirely of Pyrex glass and consisted of a lower compartment A in which the sodium was heated and an upper tube B in which the sodium vapor was condensed. The opening in a glass diaphragm was between the two tubes. A closely-fitting, water-cooled condenser was slipped over the upper tube and served to condense the sodium vapor.

The opening at O was made at the end of a 16mm. Pyrex tube, by blowing an opening approximately 3–5 mm. in diameter and then allowing the fused glass to fall in until the hole was nearly closed. By blowing the glass out at this instant, an opening of the desired size was obtained and, because of the surface tension

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[9] Heycock and Lamplough, *Proc. Chem. Soc.*, **28**, 3 (1912).

[10] A more rigorous development, involving Maxwell's distribution law and the concept of mean free path, leads to the same result. See Knudsen, *Ann. Physik*, **47**, 697 (1915).

[11] Knudsen, *Ann. Physik*, **29**, 179 (1909).

[12] Egerton, *Phil. Mag.*, **33**, 33 (1917).

[13] Egerton, *Proc. Roy. Soc.*, **722A**, 469 (1923).

of the glass, it was nearly circular. The end was then ground smooth on a plane surface in order to obtain a thin edge. A taper was also used in grinding to obtain a circular opening. When this tube was prepared it was sealed into the larger tube which later served as the sodium chamber A.

The exact area of the hole was then determined by measurement with a cathetometer the diameter of its magnified image thrown upon a screen by using a lens of 50 cm. focal length, working in a dark room. The source of light was a projection lantern The image was very sharp and no difficulty was experienced in measuring to within 0.1 mm. the diameter of the image which was approximately 30 mm. The opening itself was about 3 mm. in diameter. The chromatic aberration of the lens was eliminated by cutting down its effective area with a 12.7mm. shutter.

The outlet tube H was sealed to the upper compartment. If sealed to the lower compartment, sodium will distil into it and cause a probable unsaturation of the vapor. The outlet tube was placed in such a way that no sodium distilled into it.

A vacuum was produced in the apparatus by connecting it through a mercury trap cooled with liquid air to a mercury-vapor pump using a Cenco pump as support.

The sodium was first filtered in a vacuum through a 0.5mm. capillary tube about 3 cm. long into a reservoir bulb R. This took care of most of the oxide and the volatile impurities such as kerosene. For each determination the desired amount, usually 0.5 to 1 g., was distilled from this reservoir bulb R into the apparatus A. The sodium after such a distillation was uniformly distributed over the surface in the lower half of A. It did not get as far up as the opening O. It was not found practical to seal off the reservoir bulb directly with a vacuum in the apparatus. Helium, purified by passage over charcoal and cooled with liquid air, was therefore admitted when the sodium had solidified, and the reservoir bulb was then sealed off. Nitrogen was tried but apparently reacted sufficiently with the very active sodium surface to form a small amount of nitride, which decomposed at the higher temperature. The foregoing procedure was necessary to produce sodium free from all traces of adsorbed gases.

A determination was started by bringing the bath, already a few degrees above the desired temperature, up and around the base A to the level C. Electrically-heated oil or fused salt-baths were used. For salt the eutectic $KNO_3.NaNO_3$, m. p. 217°, was used and was very satisfactory. The sodium immediately condensed in the upper compartment B with a characteristic sky-blue color. The final adjustment of the bath to the desired temperature did not take longer than three to five minutes. The temperatures were read by means of a copper-constantan thermocouple and were regulated by hand to $\pm 0.05°$ without any difficulty. At the end of several hours the distillation was stopped by admitting nitrogen into the apparatus.

The amount of sodium that had distilled during the period *t* was determined by blowing out the side at E, taking the apparatus from the vacuum line at H, then breaking the tip at D, inverting the upper part B into a test-tube containing conductivity water and washing out the sodium with repeated rinsings. Care was taken to recover all the sodium that had distilled through O. The sodium was then determined with 0.1 *N* or 0.01 *N* hydrochloric acid as seemed best, using methyl red as an indicator. When 0.01 *N* acid was used, the end-point was matched against known standards.

The sodium could then be dissolved out of the lower tube A by alcohol admitted through E, the opening which had been blown before the apparatus was broken off at H and where the reservoir bulb would be sealed on again for the following determination.

Materials, Analytical Methods, Etc.

A commercial grade of sodium was used. Dr. G. F. Smith of this Laboratory kindly analyzed the stock from which our supply was taken, but did not detect any potassium. The presence of lithium would not be expected. The 0.1 *N* and 0.01 *N* hydrochloric acid solutions were made up by weight from conductivity water and constant-boiling hydrochloric acid which was obtained by the method of Foulk and Hollingsworth.[14] The normality of the 0.1 *N* solution was confirmed with sodium carbonate solution. Conductivity water was used at all times and methyl red was used as the indicator in the titrations.

Accuracy

It should be pointed out that the formula by which the vapor pressures are calculated is theoretically correct only for openings with sharp edges and for pressures where the mean free path, γ, of the gas is large as compared with the size of the opening. The mean free path should be large in order that molecules moving in the direction of the opening may not be diverted due to intermolecular collision. For the same reason, the opening should have a thin edge; namely, to prevent reflection of molecules. In this work the ratio λ/R ranged from 500 to 10, while the opening was made with as thin an edge as was practical.

The temperatures were determined by means of a copper-constantan thermocouple which was frequently calibrated against the boiling points of water and recrystallized naphthalene. The temperature of the thermostatic bath was regulated by hand to within $\pm 0.05°$. The temperature measurements could hardly be in error by more than 0.2° at any point.

The periods varied from three to ten hours. The shorter periods are for the higher vapor pressures and for those cases where the temperature from the beginning was usually within 2° from the desired temperature and attained this temperature within three to five minutes after the distillation was begun. Errors in the quantity t are likely to be 2% at the most.

The largest errors were in the titration of the small amounts of sodium which were distilled in the various runs. At the lower pressures this error might amount to as much as 5%.

The determinations at the higher pressures (Table II) were carried out

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[14] Foulk and Hollingsworth, This Journal, **45**, 1220 (1923).

by the method[15] of Rodebush and Dixon. A fused-nitrate bath was used as a thermostat. The temperatures were held constant within 0.5° and were determined with a platinum platinrhodium element which had been carefully calibrated against standard fixed points. The vapor-pressure determinations were reproducible to 1% of their value.

TABLE I

VAPOR PRESSURE OF SODIUM

Temp. °C.	Temp. °K.	P obs. × 10^3 Mm. of Hg	P obs. Av.	P calcd.	
				Equation 1	Equation 2
181.8	454.9	0.05040			
		.04845			
		.04950			
		.04882	0.04929	0.04372	0.04872
200.3	473.4	.1435			
		.1414			
		.1388	.1412	.1323	.1410
219.8	492.9	.3887			
		.3874	.3880	.3872	.3961
239.9	513.0	1.016			
		1.038			
		1.034			
		1.027	1.030	1.073	1.058
261.2	534.3	2.786			
		2.870			
		2.824			
		2.927	2.852	2.898	2.767

TABLE II

Temp. °C.	Temp. °C.	P obs. Mm. of Hg	P calcd. Equation 1
514	787	5.56	5.61
536	809	8.42	8.59
548	821	10.98	10.74
550	823	11.05	11.13
597	870	24.92	24.91
883[a]	1156	760.00	760.00

[a] See Ref. 9.

The data for sodium are shown in Tables I and II, including the boiling-point determination of Heycock and Lamplough. Col. 5 contains the values calibrated from the equation

$$\log p = -5922/T - 1.6184 \log T + 12.9605 \qquad (1)$$

This equation is purely empirical but if we accept the boiling-point determination as accurate we may calculate vapor pressures with confidence over the entire included range of temperature.

On the other hand we must not assume that Equation 1 is the only one that may be found to fit the data. The coefficient of log T is presumably equal to $\Delta C_p/R$, but we should not be justified in calculating ΔC_p from

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[15] Not yet published.

this equation unless our data were very accurate and exactly fitted by Equation 1. In the absence of accurate data for ΔC_p, the vapor-pressure data at the higher temperatures are practically useless for the calculation of thermal quantities. On the other hand, we find that the measurements at the lower pressures by the Knudsen method may be fitted by the simpler equation $\log p = -(5370/T) + 7.4925$. Here ΔC_p is neglected, a procedure that is justifiable if the temperature interval is short. From the equation we calculate the heat of vaporization of sodium to be 24,600 cal. near the melting point.

The Entropy of Sodium Vapor

The entropy of solid sodium at the melting point 97.6° is calculated to be 13.99. From the data of Griffiths[16] the entropy of fusion is 1.17. The entropy of vaporization to 1 atmosphere at the melting point is from the equation

$$\Delta S = 2.3\, R \times 7.4925 - R\, ln\, 760 = 21.1 \tag{2}$$

Subtracting 1.09 units for the reduction to 298.1° K. we have $S_{298.1} = 35.71$, as compared with a value of 35.35 predicted by the Tetrode equation. We have neglected ΔC_p in this calculation. Presumably it is about 2 calories. If we were to take account of it in the extrapolation of Equation 2 to the melting point we should find a value for S_{298} several tenths of a unit higher. On the other hand, the heat-capacity data for metallic sodium are not complete at low temperatures and it seems likely that the value we have used for the solid at the melting point is too high. Hence, we shall adopt as the best value, $S_{(vapor\ 298)} = 35.7 \pm 0.5$.

Summary

The vapor pressure of sodium has been measured over the temperature range 181.8° – 597°.

An equation has been fitted to the vapor-pressure data from 180° to the boiling point.

The entropy of sodium vapor at 298° K. and 1 atmosphere is calculated to be 35.7 ± 0.5.

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[16] Griffiths, *Proc. Roy. Soc.*, **89A**, 561 (1914).