

TABLE III.

Partial volumes measured.....	23.852	8.468	10.800	1.201
	24.942	11.379	5.268	0.219
	28.443	8.589	20.791	
			29.671	
			7.647	
			24.690	
Sum.....	77.237	28.436	98.867	1.420
Direct determination of total volume.....	77.244	28.443	98.881	1.413

The data presented in the above tables indicate a percentage accuracy on a sample of 100 cc. which is comparable with the accuracy of good titrimetric determinations.

Since the size and shape of the container in which the gas is measured are determined only by convenience, the method is obviously suited to the measurement of much larger volumes of gas than were here determined. Water can, of course, be used as the confining liquid with the usual limitations on account of solubility.

The apparatus can also be easily adapted as an accurate and convenient gas volumeter for determining the amount of gas evolved from a solid or liquid by any chemical reaction. For this purpose the weight of sample taken and the amount of gas confined in the compensator may be so related that the weight of confining liquid will be a simple multiple of the percentage of the constituent to be determined.

#### Summary.

An apparatus for conveniently determining small quantities of gas by weighing the confining liquid displaced is described and its percentage accuracy is shown to be comparable with the general accuracy of good titrimetric measurements.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, ORDNANCE DEPARTMENT.]

### THE ENTROPY OF GASES.

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From a thermodynamic point of view, the problem of chemical affinity may be considered as completely solved, as soon as we have determined the heat content and the entropy content of all the reacting substances in which we are interested. The solution of this important task has been greatly simplified by the work of Nernst and Planck in introducing the so-called third law of thermodynamics, which states that the entropy content of solids and liquids becomes zero at the absolute zero of temperature. This has made possible a determination of the entropy content of *solids* and *liquids* at any temperature merely from a knowledge of specific

heat data. The next step in this field of thermodynamic chemistry is a consideration of the underlying principles determining the entropy of *gases* and *solutes*.

Considerable theoretical speculation on the problem of the entropy of monatomic gases, or on the equivalent problem of determining Nernst's so-called chemical constants, has already been done by Sackur,<sup>1</sup> Tetrode,<sup>2</sup> Stern,<sup>3</sup> Keesom,<sup>4</sup> Nernst,<sup>5</sup> Ratnowsky<sup>6</sup> and Lindemann.<sup>7</sup> These investigators have obtained a considerable measure of agreement in their conclusions in spite of the fact that they have based their work on a variety of assumptions which are hard to disentangle, and sometimes conflicting. Comparisons of experimental data with the results of these theoretical predictions have been made by Nernst<sup>8</sup> and Egerton.<sup>9</sup>

The purpose of the present paper is first to derive an equation for the entropy of a monatomic gas in a new and very simple way, making use of the author's theory of similitude,<sup>10</sup> and then to compare the predicted results with the relatively accurate values of the entropies of the elements which have been presented by Lewis and Gibson.<sup>11</sup> It should be noted in this connection that the entropy values of Lewis and Gibson have been obtained from plots of actual specific heat data and hence provide a more satisfactory basis of comparison than was available to Nernst<sup>12</sup> and Egerton.

#### 1. General Equation for the Entropy of a Perfect Monatomic Gas.—

Since the heat capacity per mol at constant pressure for a perfect monatomic gas is exactly equal to  $(5/2)R$  and the heat absorbed when the pressure is changed reversibly at temperature  $T$  from  $p_1$  to  $p_2$  is exactly equal to  $RT \ln(p_1/p_2)$ , we can evidently write as an expression for the entropy of a perfect monatomic gas at temperature  $T$  and pressure  $p$ ,

$$S = S_1 + 5/2 R \ln T - R \ln p, \quad (1)$$

where  $S_1$  is the entropy of the gas at unit temperature and unit pressure.

An examination of this equation shows that the problem of determining

<sup>1</sup> Sackur, *Ann. phys.*, 36, 598 (1911); 40, 67 (1913).

<sup>2</sup> Tetrode, *ibid.*, 33, 434 (1912).

<sup>3</sup> Stern, *Physik. Z.*, 14, 629 (1913); *Ann. Phys.*, 44, 497 (1914).

<sup>4</sup> Keesom, *Physik. Z.*, 15, 217 (1914).

<sup>5</sup> Nernst, *Ver. deut. physik. Ges.*, 18, 83 (1916).

<sup>6</sup> Ratnowsky, *ibid.*, 18, 263 (1916).

<sup>7</sup> Lindemann, *Phil. Mag.*, 38, 173 (1919); 39, 21 (1920).

<sup>8</sup> Nernst, "Die Theoretischen und Experimentellen Grundlagen des neuen Wärmesatzes" (1918).

<sup>9</sup> Egerton, *ibid.*, 39, 1 (1920).

<sup>10</sup> Tolman, *Phys. Rev.*, 3, 244 (1914); 4, 145 (1914); 6, 219 (1915); 8, 8 (1916); 9, 237 (1917).

<sup>11</sup> Lewis and Gibson, *THIS JOURNAL*, 39, 2554 (1917).

<sup>12</sup> A number of additional gases other than those considered by Nernst and Egerton will be treated in this paper.

the entropy of perfect monatomic gases will be completely solved as soon as we have some means of predicting the value of the undetermined quantity  $S_1$ . This quantity will obviously depend in the first place on the units of entropy, temperature and pressure employed, and in the second place may depend on the properties of the particular gas which is under consideration. Since the gases to be considered are by hypothesis both *perfect* and *monatomic*, they can theoretically consist only of non-attracting, point particles and hence such gases can differ from each other only in the mass of these point particles, *i. e.*, in their molecular weight  $m$ . Under these circumstances the only property of the gas upon which  $S_1$  can depend is the molecular weight  $m$ . Hence we can obviously re-write Equation 1:

$$S = \phi(m) + 5/2 R \ln T - R \ln p \quad (2)$$

where  $\phi$  is some functional relation whose form we wish to determine.

2. **Application of Theory of Similitude.**—The theory of similitude,<sup>1</sup> requires that all the general equations of physics must be completely invariant when the different physical variables contained in the equation are transformed in accordance with a particular set of transformation equations which have been developed from the theory. For the quantities involved in our equation, *i. e.*, entropy (per mol)  $S$ , mass (per mol)  $m$ , heat capacity (per mol)  $R$ , temperature  $T$ , and pressure  $p$ , the transformation equations developed from the theory of similitude are as follows:

$$S = S' \quad m = xm' \quad R = R' \quad T = xT' \quad p = x^4p' \quad (3)$$

where  $x$  may be any pure number.

Substituting in Equation 2 we obtain,

$$S' = \phi(xm') + 5/2 R' \ln xT' - R' \ln x^4p'. \quad (4)$$

In accordance with the invariance demanded by the theory of similitude the function  $\phi$  must be of such a form that all the  $x$ 's in (4) shall cancel out, and by inspection we see that this can only be true when  $\phi$  has the form

$$\phi(m) = R \ln a(m)^{3/2} \quad (5)$$

where  $a$  is a general constant independent of the gas. Substituting in Equation 2 we obtain as our final equation,

$$S = 3/2 R \ln m + 5/2 R \ln T - R \ln p + S_0 \quad (6)$$

where the quantity  $S_0 = 3/2 R \ln a$  is a general constant independent of the particular gas.

We have thus obtained in a very simple way a general equation for the entropy of perfect monatomic gases. In a later section of the article we shall compare the available experimental data with the predictions of this equation.

<sup>1</sup> *Loc. cit.*

3. **Other Theoretical Methods of Attack.**—Equation 5 or its equivalent has been derived by several investigators.

Lindemann<sup>1</sup> has applied dimensional reasoning to the equivalent problem of determining the relation between the molecular weight  $m$  and Nernst's chemical constant  $C$  which is directly related to our quantity  $S_1$ , and has arrived at conclusions that are in agreement with ours. It is important to point out, however, that the successful application of dimensional reasoning to this problem requires additional and arbitrary assumptions over those necessary for solving the problem by the theory of similitude. Referring again to Equation 2 we see, since  $S$  and  $R$  both have the same dimensions, that  $\phi(m)$  must have the dimensions of  $R \ln pT^{-5/2}$  or written in the form of a dimensional equation

$$[\phi] = [ml^2t^{-2}T^{-1} \ln ml^{-1}t^{-2}T^{-5/2}].$$

Now, it is obvious that no function of  $m$  alone can have these required dimensions, and hence since we have already come to the conclusion that  $m$  is the only "dimensionable variable" entering the function  $\phi(m)$ , it is evident that  $\phi(m)$  must also include one or more "dimensional constants." Since, however, we have no way of knowing beforehand what these "dimensional constants" may be, we have no way of solving the problem. In order to try to meet this difficulty, we could follow Lindemann<sup>1</sup> by making the additional assumption that the only dimensional constants involved in  $\phi(m)$  are Planck's constant  $h$  and Boltzman's constant  $k = R/N$  and would then find it possible to derive our final equation (6), by finding the only combination of  $m$ ,  $h$  and  $k$  which has the dimensions required by Equation 7. This added assumption seems, however, relatively arbitrary and greatly reduces the value of the attempted dimensional treatment.

Sackur, Tetrode, Stern, Keesom, Nernst and Ratnowsky<sup>2</sup> have all also derived equations of the form (6) for the entropy of a perfect monatomic gas. Their work is based on a variety of assumptions which are rather difficult to disentangle and they do not come to complete agreement as to the magnitude of the universal constant which we have called  $S_0$ ; they all agree, however, that the entropy of a monatomic gas depends on the atomic weight in the way predicted in our equation. To give a partial statement as to the kind of assumptions which they have employed, Sackur's first derivation was based on the Sommerfeld hypothesis that every element of action in the universe is some multiple of the fundamental constant of action  $h$ . In his later derivation he abandons this hypothesis on account of the fact that action is the product of two quantities, energy and time, both of which are presumably continuous in nature, and bases his conclusions on what he conceives to be a fundamental analysis of the

<sup>1</sup> *Loc. cit.*

<sup>2</sup> All *loc. cit.*

significance of  $h$ . Tetrode bases his work on the assumption that the volume  $\sigma$ , of the "cells of equal probability" into which we can divide the  $2n$  dimensional space familiarly used in the considerations of statistical mechanics for plotting the values of the  $n$  generalized coördinates and  $n$  generalized momenta belonging to the elements of the system, can be put equal to  $z^h$  where  $h$  is Planck's constant and  $z$  is a pure number. Stern's value for the entropy of a perfect monatomic gas is obtained by considering the entropy increase in heating a solid from the absolute zero to a point where Dulong and Petit's law holds, and then vaporizing. To determine the entropy increase in heating the solid he makes use of the Planck-Einstein formula for the specific heat of a solid with a single frequency of vibration and to determine the entropy of evaporation he makes use of theoretical molecular speculations. The particular and improbable assumptions as to the nature of the solid are found to disappear from the final result. Keesom, Nernst and Ratnowsky all assume a so-called "nullpunkt energie"  $\epsilon_0$  for the lower value of the energy at the absolute zero still associated with a degree of freedom of frequency  $\nu$ . This "nullpunkt energie" in the Nernst treatment is in equilibrium with radiant energy in the ether. On rise of temperature, energy is drawn not only from the surroundings but also from the reservoir of "nullpunkt energie" and the principle of the conservation of energy becomes merely statistically true rather than true for the individual elements of the system. It is evident that the theories in question (like so much of quantum theory) are still in their birth-pangs. For the time being, the simple although non-mechanistic treatment afforded by the theory of similitude may prove useful.

**4. Entropy of Gases in General.**—The above treatment provides primarily a method for calculating the entropy of gases which are monatomic. The work of Eucken, however, has shown that hydrogen has only 3 degrees of freedom at low temperatures, and we are led to expect that all gases will behave as though monatomic at low enough temperatures. This will permit us to calculate the entropy of any gas at any temperature as soon as we obtain the necessary specific heat data bridging over the gap between very low and moderate temperatures. In the case of hydrogen such a calculation is already possible, and in the sequel we shall show the agreement between the experimental and predicted results for this gas.

**5. Calculation of Results.**—Returning to our fundamental equation (6), we have

$$S = 3/2 R \ln m + 5/2 R \ln T - R \ln p + S_0 \quad (6)$$

where  $S_0$  is a constant independent of the nature of the gas. Since we shall use this equation for calculating entropies always at 25° and one

atm. pressure,  $T$  and  $p$  become constant and the equation can be rewritten for our purposes in the form

$$S_{298} = 6.87 \log m + C.$$

*Helium.*—We shall choose the gas helium for determining the value of  $C$ . In accordance with Lewis and Gibson,<sup>1</sup> we shall take  $S_{298} = 29.2$  and shall take  $m = 4.00$ . We obtain  $C = 25.1$ , and may now write, for any monatomic gas of molecular weight,  $m$ ,

$$S_{298} = 6.87 \log m + 25.1. \quad (7)$$

*Argon.*—For argon Lewis and Gibson<sup>1</sup> give the value  $S_{298} = 36.4$ , while a substitution of  $m = 40.0$  gives  $S_{298} = 36.1$  a satisfactory check.

*Mercury, Cadmium, Zinc, Platinum, Molybdenum, Tungsten.*—The vapor pressures for a number of metals which give monatomic gases have been determined and expressed in the literature by a formula of the Hertz type,

$$\log p(\text{mm.}) = -A/T + B \log T + C. \quad (8)$$

Assuming this formula to be accurate enough for purposes of extrapolation, it may be used for determining the change in entropy at  $298^\circ$  when the metal is evaporated at its vapor pressure and then compressed to one atmosphere. Changing to natural logarithms and to pressures in atmospheres we may write in place of Equation 8,

$$\ln p(\text{atm.}) = -2.3 A/T + B \ln T + 2.3 C - 2.3 \log 760. \quad (9)$$

Differentiating and substituting into the Clausius equation,  $d \ln p/d T = L/RT^2$ , we obtain

$$L/T = (2.3 AR/T) + BR \quad (10)$$

and this is the entropy increase when we evaporate at temperature  $T$  to form vapor at the vapor pressure  $p$ . Adding the quantity  $R \ln p$ , which is the increase in entropy when we change to a pressure of one atmosphere, and making use of Equation 9, we obtain,

$$\Delta S = L/T + R \ln p = BR + BR \ln T + 2.3 CR - 2.3 R \log 760.$$

Since we shall be interested in the value of  $\Delta S$  at  $298^\circ$  absolute, we may substitute  $T = 298$ ,  $R = 1.99$  and obtain,

$$\Delta S_{298} = 13.33 B + 4.58 C - 13.65. \quad (11)$$

This equation gives us the increase in entropy when one mol of vapor at atmospheric pressure is formed from the condensed phase at  $298^\circ$  absolute. We may apply it to the following vapor pressure data:

*Mercury.*—Vapor pressure measurements by Knudsen,<sup>2</sup> between  $273^\circ$  and  $323^\circ$  absolute:

$$\log p(\text{mm.}) = (-3342.26/T) - 0.847 \log T + 10.5724.$$

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Knudsen, *Ann. phys.*, **29**, 179 (1909).

*Cadmium*.—Vapor pressure measurements by Egerton<sup>1</sup> between 411.2 and 545.5° absolute:

$$\log p(\text{mm.}) = (-6060/T) - 0.5 \log T + 10.5979.$$

*Zinc*.—Vapor pressure measurements by Egerton,<sup>1</sup> between 529.8 and 636.0° absolute:

$$\log p(\text{mm.}) = (-7176/T) - 0.5 \log T + 10.9433.$$

*Platinum*.—Vapor pressure measurements by Langmuir and MacKay,<sup>2</sup> between 1682 and 2000 absolute:

$$\log p(\text{mm.}) = (-27800/T) - 1.26 \log T + 14.09.$$

*Molybdenum*.—Vapor pressure measurements by Langmuir and MacKay,<sup>2</sup> between 1994 and 2373 absolute:

$$\log p(\text{mm.}) = (-38600/T) - 1.26 \log T + 17.354.$$

*Tungsten*.—Vapor pressure measurements by Langmuir,<sup>3</sup> between 2440 and 2930° absolute:

$$\log p(\text{mm.}) = (-47440/T) - 0.9 \log T + 15.502.$$

Applying Equation 11 to the above data, adding the values given by Lewis and Gibson<sup>4</sup> for the entropy of the condensed phase at 298° absolute, and comparing with the results of the theoretical Equation (7), we obtain,

	Lewis-Gibson.	$\Delta S_{298^\circ}$ Equation 11.	$S_{298^\circ}$ Experimental.	$S_{298^\circ}$ Theoretical.
Mercury.....	17.8	23.3	41.1	40.9
Cadmium.....	11.6	28.2	39.8	39.2
Zinc.....	9.8	29.9	39.7	37.6
Platinum.....	10.0	33.9	43.9	40.8
Molybdenum.....	7.5	48.9	56.4	38.7
Tungsten.....	8.4	45.3	53.7	40.7

There is good agreement between the experimental and theoretical values of entropy except for molybdenum and tungsten. This lack of good agreement is not surprising, in view of the vapor pressure extrapolation over a range of 2000°.

*Monatomic Bromine, Iodine and Hydrogen*.—Free energy and entropy are connected by the equation,

$$\Delta S = (\Delta H - \Delta F)/T \tag{12}$$

where  $\Delta S$  is the increase in entropy accompanying a reaction at temperature  $T$ ,  $\Delta H$  being the increase in heat content and  $\Delta F$ , the increase in free energy. Using the nomenclature of Lewis we may write,

$$\Delta H = \Delta H_0 + \Delta \Gamma_0 T + \Delta \Gamma_1/2 T^2 + \Delta \Gamma_2/3 T^3 + \dots$$

$$\Delta F = \Delta H_0 - \Delta \Gamma_0 T \ln T - \Delta \Gamma_1/2 T^2 - \Delta \Gamma_2/6 T^3 \dots + IT$$

<sup>1</sup> Egerton, *Phil. Mag.*, 33, 333 (1917).

<sup>2</sup> Langmuir and MacKay, *Phys. Rev.*, 4, 377 (1914).

<sup>3</sup> Langmuir, *ibid.*, 2, 329 (1913).

<sup>4</sup> *Loc. cit.*

where  $I$  is an integration constant and the  $\Delta\Gamma$  terms are dependent in a familiar way upon heat capacities. Substituting into Equation 12 we obtain,

$$\Delta S = \Delta\Gamma_0 + \Delta\Gamma_0 \ln T + \Delta\Gamma_1 T + \Delta\Gamma_2/2 T^2 + \dots - I. \quad (13)$$

This equation can be applied to the following free energy data.

*Bromine*.—Lewis and Randall<sup>1</sup> give the following free energy equation for the reaction  $\text{Br}(l.) = \text{Br}(g.)$  based on dissociation measurements between 1073 and 1323° absolute.

$$\Delta F = 31425 + 3.05 T \ln T + 0.001 T^2 - 48.14 T.$$

*Iodine*.—Lewis and Randall<sup>2</sup> give the following free energy equation for the reaction  $I(s.) = I(g.)$  based on dissociation measurements between 1073 and 1473° absolute.

$$\Delta F = 26275 + 1.60 T \ln T - 40.36 T.$$

*Hydrogen*.—Lewis and Randall<sup>3</sup> give the following free energy equation for the reaction  $H_2 = 2H$  based on dissociation measurements between 2500 and 3000° absolute.

$$\Delta F = 61000 - 3.5 T \ln T + 0.00045 T^2 + 20.2 T.$$

Applying Equation 13 to the above data, using  $T = 298$ , adding the values given by Lewis and Gibson,<sup>4</sup> for the entropy of the undissociated gas at 298° absolute, and comparing with the results of the theoretical equation (7) we obtain,

	Lewis-Gibson.	$\Delta S$ 298°. Equation 13.	$S$ 298°. Experimental.	$S$ 298°. Theoretical.
Bromine (Br).....	18.5	27.1	45.6	38.2
Iodine (I).....	15.7	29.6	45.3	39.6
Hydrogen (H)....	15.9	1.5	17.4	25.1

The relatively poor agreement is probably due to the wide extrapolation necessary from temperatures where the equilibrium could be measured.

*Diatomic Hydrogen*.—As already stated, our theoretical equation not only makes possible a prediction of the entropy of monatomic gases, but since all gases become monatomic at low temperatures, permits a treatment of all gases as soon as the necessary specific heat data are available. In the case of hydrogen such data have been obtained by Eucken,<sup>5</sup> Plotting Eucken's data for the specific heat of hydrogen against the logarithm of the temperature, it was found that the entropy of hydrogen ( $H_2$ ) at 298° is 1.4 units greater than it would be if it had remained a monatomic gas way up to that temperature. Using our theoretical Equation (7) for the entropy of a monatomic gas and adding 1.4 we get

<sup>1</sup> Lewis and Randall, *THIS JOURNAL*, 38, 2348 (1916).

<sup>2</sup> Lewis and Randall, *ibid.*, 36, 2259 (1914).

<sup>3</sup> Lewis and Randall, *ibid.*, 36, 1969 (1914).

<sup>4</sup> *Loc. cit.*

<sup>5</sup> Eucken, *Sitzb. kgl. preuss. Akad.*, 1912, 148.



28.6 as compared with the two values of Lewis and Gibson 29.4 and 31.8, a satisfactory check, although they believe the higher value is the more reliable.

**6. Summary of Data.**—The following table presents a comparison of the experimental results for the entropy of gases at one atmosphere and 298° absolute, and the theoretical results predicted with the help of the equation,

$$S = (3/2) R \ln m + (5/2) R \ln T - R \ln p + S_0 \\ = 6.87 \log m + 25.1 \text{ (at 1 atm. and 298° abs.)}.$$

The second column states the range of temperature over which extrapolation has to be made in order to compare the results, and these results are arranged in the order of the uncertainty introduced by this factor.

Gas.	Range over which extrapolation was made. °.	$S_{298^\circ}$ . Experimental.	$S_{298^\circ}$ . Theoretical.	Diff.
Helium.....	....	29.2	....	....
Argon.....	None	36.4	36.1	0.3
Mercury.....	None	41.1	40.9	0.2
Hydrogen (H <sub>2</sub> )...	None	31.8(29.4)	28.6	3.2
Cadmium.....	150	39.8	39.2	0.6
Zinc.....	300	39.7	37.6	2.1
Bromine.....	900	45.6	38.2	7.4
Iodine.....	900	45.3	39.6	5.7
Platinum.....	1500	43.9	40.8	3.1
Molybdenum....	1700	56.4	38.7	17.7
Tungsten.....	2100	53.7	40.7	13.0
Hydrogen (H)....	2500	17.4	25.1	7.7

The agreement between the experimental and theoretical values is very close in cases where wide extrapolation does not have to be made and is probably within the experimental error in all cases. It should also be noted that the nature of the experimental results alone is enough to show that entropy of gases is certainly not entirely a fortuitous matter.

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