

Summary.

1. Iodate may be determined accurately by reducing it with an excess of known iodide solution in dil. sulfuric acid, and titrating the excess with permanganate solution, electrometrically.
2. Iodide can be titrated directly with iodate in dil. sulfuric acid, by the electrometric method.
3. Hydrochloric acid may not be substituted for sulfuric except within very narrow limits of concentration in the determination of iodide with either permanganate or iodate.
4. These determinations may be made in the presence of chloride not exceeding about 0.1 *N*, or in presence of nitric acid of higher concentration if it contains only traces of nitrous acid.
5. Silver may be accurately determined electrometrically with pure iodide and permanganate solution.
6. Pure silver may be used as a standard in determining the values of both iodide and permanganate.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]¹

THE PRINCIPLE OF SIMILITUDE AND THE ENTROPY OF POLYATOMIC GASES.

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In a previous article,² the author has shown the possibility of using the principle of similitude for predicting the relation between the entropy of a monatomic gas and its molecular weight. It is possible to extend the mode of attack so as to treat diatomic and polyatomic gases, provided they can be thought of as composed of rigid particles having a definite molecular weight, and definite moments of inertia around their centers of gravity.

The purposes of the present article are, (1) to give a brief introduction to the theory of similitude³ or relativity of size, using a method of pre-

¹ Published by permission of the Chief of Ordnance.

² Tolman, *THIS JOURNAL*, **42**, 1185 (1920).

³ Tolman, *Phys. Rev.*, **3**, 244 (1914); **4**, 145 (1914); **6**, 219 (1915); **8**, 8 (1916); **9**, 237 (1917); *Gen. Elec. Rev.*, **23**, 486 (1920). See also Karrer, *Phys. Rev.*, **9**, 290 (1917); Davis, *Science*, **50**, 338 (1919).

sentation which is perhaps somewhat simpler than those previously employed; (2) to derive equations connecting the entropy of a perfect gas composed of rigid diatomic or polyatomic molecules, with temperature, pressure, molecular weight and the moments of inertia of the molecule; (3) to compare these equations with those of Sackur,¹ Tetrode,² Schames³ and Latimer,⁴ and finally (4) to compare the equations with the available experimental data.

It will be found that the equations agree with the available experimental data, and agree with the equations of Sackur, Tetrode and Schames, but disagree with that proposed by Latimer for the case of diatomic gases.

The Theory of Similitude or Relativity of Size.

The fundamental idea of the theory of similitude or relativity of size arises from the fact that the size of an object is evidently merely a relative matter. For example, if we desire to specify the length of a given object we can say that it is so many times as long as a standard meter-stick, or a yard-stick, or a foot-rule, or any other measuring rod which we may select. To speak of the absolute length of the object, however, would be meaningless. If this consideration is correct, it would seem that the fundamental general equations of physics should be independent of the choice of any particular length as the standard length in terms of which all measurements shall be made.

We may put this idea in the form of a definite postulate, upon which the theory of the relativity of size may be founded, as follows. *A change is possible in the magnitudes of the standards for the measurement of the different quantities of physics, including any desired change in the standard of length, which will leave all the general equations of physics absolutely invariant, both as to form and numerical content.*

By the term "general" equations of physics we mean equations that describe classes of phenomena rather than equations that describe merely one particular phenomenon. Consider, for example, the equation for the relation between the circumference and diameter of a circle, $C = \pi D$. This is a "general" equation, applying to all circles, and is absolutely invariant both as to form and as to the numerical value of the quantity π , for any change in the standard of length. A statement, however, as to the circumference of some one particular circle, say, $C = 24$,

¹ Sackur, *Ann. Physik*, **40**, 87 (1913).

² Tetrode, *Amster. Proc.*, **17**, 1167 (1915).

³ Schames, *Physik. Z.*, **21**, 38 (1920).

⁴ Latimer, *THIS JOURNAL*, **43**, 818 (1921). Latimer's article was sent by the Editor to the present writer as a referee before publication. Grateful acknowledgment is made for the stimulus thereby received and for the advance opportunity of using Latimer's figures for the experimental values of the entropies of diatomic gases.

would be a "special" equation and, of course, would not be invariant in numerical content if we changed our standard of length.

The Transformation Equations.—Returning now to our fundamental postulate, it must be possible to find a set of transformation equations for the quantities of physics, which can be substituted into all the general equations of physics and yet leave them absolutely unchanged both as to form and as to numerical content. Since the transformation must correspond to any desired change in the standard of length, we may write as the first of our transformation equations,

$$l = \alpha l' \tag{1}$$

where α can be any desired number.

Substituting the value for l given by this transformation equation into any equation of physics, obviously means that we have changed to a new standard of length α times as long as our previous standard, and the values of length, l' , occurring in the transformed equation will be the values that would have been obtained if the observer had used the longer standard of length. Our fundamental postulate requires now that the substitution of this equation, together with the similar equations to be obtained for the other quantities of physics, shall leave all the general equations of physics absolutely invariant both as to form and as to numerical content.

In order to find the further transformation equations for all the other quantities of physics, it will only be necessary in the first instance to have transformation equations for the five fundamental kinds of quantity, length, time, mass, quantity of electricity, and entropy, and then, since all the quantities of physics can be defined in terms of these fundamental quantities, it will be possible from purely dimensional considerations alone, to determine the transformation equations for all the quantities of physics.

Starting with the above transformation equation for length l , we may obtain transformation equations for the four further quantities time t , mass m , quantity of electricity e , and entropy S by considering the following four general physical equations, all of which must be invariant when the transformation equations in question are substituted.

The equation for the way a light disturbance spreads out in free space,

$$dx^2 + dy^2 + dz^2 = c_2^2 dt^2. \tag{A}$$

The fundamental equation stating that the charge on a given body is equal to a constant ϵ , times the number of free electrons n on the body,

$$e = \epsilon n. \tag{B}$$

Coulomb's law for the force $f = d/dt(m dl/dt)$ acting on a particle of mass m and charge e_1 , under the influence of another charge e_2 at a distance l .

$$\frac{d}{dt} \left(m \frac{dl}{dt} \right) = K \frac{e_1 e_2}{l^2}. \quad (\text{C})$$

And the fundamental relation of Boltzmann and Planck connecting the entropies of an isolated system in two different states, S_1 and S_2 with the probabilities of these two states W_1 and W_2 ,

$$S_1 - S_2 = k \ln \frac{W_1}{W_2}. \quad (\text{D})$$

We are now ready to derive the transformation equations for time, mass, quantity of electricity and entropy.

To derive the equation for time, we note that Equation (A) must be unchanged in form and numerical content when we apply the transformation equations. The application of Equation (1) to the quantities of length involved will change Equation (A) into,

$$\alpha^2(dx'^2 + dy'^2 + dz'^2) = c^2 dt^2.$$

If the equation is to retain its original numerical content (*i. e.*, an unchanged value for the constant c) when we introduce the further transformation equation for time, it is evident that this equation must have the form,

$$t = \alpha t'. \quad (2)$$

Turning now to Equation (B), we may derive the transformation equation for quantity of electricity, by noting that the value of a number of discrete objects cannot depend on the standards of measurement and hence the number of electrons n will not be changed by the transformation. This being true, Equation (B) can only be invariant in numerical content (*i. e.*, in the value of the constant ϵ) if the transformation equation for quantity of electricity has the form,

$$e = e'. \quad (3)$$

Turning to Equation (C) and applying the transformation equations already obtained for length, time and quantity of electricity we obtain,

$$\frac{d}{dt'} \left(m \frac{dl'}{dt'} \right) = \frac{K}{\alpha} \frac{e_1' e_2'}{l'^2}.$$

If this equation is to resume its former numerical content (*i. e.*, the same value for the constant K) when we introduce the further transformation equation for mass m , it is evident that the desired equation must have the form,

$$m = \frac{m'}{\alpha}. \quad (4)$$

Turning finally to Equation (D),¹ we note that the ratio of the two prob-

¹ A simple presentation of the justification for Equation (D),

$$S_1 - S_2 = k \ln \frac{W_1}{W_2},$$

will be found among other places in Planck's "Vorlesungen über die Wärmestrahlung."

The derivation is based solely on the assumption that there must be *some* general

abilities W_1 and W_2 is equal to the ratio of the time intervals t_1 and t_2 in which the isolated system would be found in the two different states after a long period of observation, hence we may write,

$$S_1 - S_2 = k \ln \frac{t_1}{t_2}.$$

Noting the transformation equation already obtained for time, it is evident that this equation can only remain invariant in numerical content (*i. e.*, in the value of the constant k) if the transformation equation for entropy has the form,

$$S = S' \quad (5)$$

Having now obtained the transformation equations for the five fundamental kinds of quantity, the transformation equations for further quantities can be obtained by considering their dimensions. For example, since velocity u has the dimensions of length over time,

$$[u] = [lt^{-1}]$$

it is evident from (1) and (2) that the transformation equation for velocity will be,

$$u = u' \quad (6)$$

Since energy has the dimensions of mass times velocity squared,

$$[E] = [ml^2t^{-2}]$$

it is evident from (1), (2) and (4) that the transformation equation for energy will be,

$$E = \frac{E'}{\alpha}. \quad (7)$$

Proceeding in this manner, the following table of transformation equations can be constructed.

Quantity.	Dimensions.	Transformation equations.
Length l	$[l]$	$l = \alpha l'$ (1)
Time t	$[t]$	$t = \alpha t'$ (2)
Quantity of electricity e	$[e]$	$e = e'$ (3)
Mass m	$[m]$	$m = \alpha^{-1} m'$ (4)
Entropy S	$[S]$	$S = S'$ (5)
Velocity u	$[lt^{-1}]$	$u = u'$ (6)
Energy E	$[ml^2t^{-2}]$	$E = \alpha^{-1} E'$ (7)

relation between the entropy of a system and its probability, and the further consideration that the entropies S and S' of two systems must be added to obtain their total entropy, while their probabilities W and W' must be multiplied in order to obtain the combined probability. The only difficulties that have arisen in connection with the application of Equation (D) have been due to uncertainties as to the proper method of specifying probabilities W . In the case of an *isolated* system, however, which can spontaneously assume for such periods as it "desires" two different states (1) and (2), it is evident that, however, we may later decide to specify probabilities, these probabilities must be in the same ratio as the time intervals in which the system will be found in the two different states.

Quantity.	Dimensions.	Transformation equations.
Volume v	$[l^3]$	$v = \alpha^3 v'$ (8)
Force f	$[mlt^{-2}]$	$f = \alpha^{-2} f'$ (9)
Pressure p	$[ml^{-1}t^{-2}]$	$p = \alpha^{-4} p'$ (10)
Moment of inertia I	$[ml^2]$	$I = \alpha I'$ (11)
Temperature T	$[ml^2t^{-2}S^{-1}]$	$T = \alpha^{-1} T'$ (12)

The Entropy of Gases.

The Entropy of a Monatomic Gas.—Consider a perfect monatomic gas, composed of point particles of mass m . Since the molal specific heat at constant pressure of such a gas is exactly $5/2R$ the entropy of one mol of this gas at any temperature T and pressure p will be given by the well-known thermodynamic formula,

$$S = 5/2R \ln T - R \ln p + S_0$$

where S_0 is a constant for a given gas.

If we consider that two such gases can differ from each other only in the mass of the particles, that is, in molecular weight m , it is evident that S_0 can only be a function of m , so that we may write

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

If this is one of the general equations of physics, it must remain invariant as to form and as to numerical content (*i. e.*, the value of the constant R) when we substitute the transformation equations found above. We obtain,

$$S' = 5/2R \ln \frac{T'}{\alpha} - R \ln \frac{p'}{\alpha^4} + \phi\left(\frac{m'}{\alpha}\right).$$

It is evident that the condition of invariance can only be met if the function $\phi(m)$ has the form,

$$\phi(m) = 3/2R \ln m + S_1,$$

where S_1 is the *same* constant for all monatomic gases. We obtain as our equation for the entropy of a perfect monatomic gas

$$S = 5/2R \ln T - R \ln p + 3/2R \ln m + S_1. \quad (13)$$

The Entropy of a Diatomic Gas.—Consider an ideal diatomic gas, composed of molecules containing two atoms rigidly bound together at a fixed distance. At temperatures high enough so that the molal specific heat at constant pressure is exactly $7/2R$, corresponding to the two *rotational* degrees of freedom added to the translational degrees of freedom for a monatomic gas, we may write for the entropy per mol,

$$S = 7/2R \ln T - R \ln p + S_0$$

where S_0 is a constant for a given gas.

The molecule now under consideration differs from monatomic molecules in that it is capable of picking up rotational energy with reference to two axes which are at right angles to the line joining the atoms. The moments of inertia I and J around these two axes will be equal,

$$I = J$$

and hence if we consider that the entropy of such an ideal diatomic gas is solely a function of temperature T , pressure p , molecular weight m and the moments of inertia $I = J$, we may write,

$$S = 7/2R \ln T - R \ln p + \phi(m, I).$$

If this is one of the general equations of physics, it must remain invariant as to form and numerical content when we substitute our transformation equations. We obtain,

$$S' = 7/2R \ln \frac{I'}{\alpha} - R \ln \frac{p'}{\alpha^4} + \phi\left(\frac{m'}{\alpha}, \alpha I'\right).$$

If now we make the reasonable assumption that the molecular weight enters into this equation in the same way as for a monatomic gas, it is evident that our desired invariance can only be obtained if $\phi(m, I)$ has the form,

$$\phi(m, I) = 3/2R \ln m + R \ln I + S_2,$$

where S_2 is a constant independent of the particular diatomic gas. We obtain as our equation for the entropy of our ideal diatomic gas,

$$S = 7/2R \ln T - R \ln p + 3/2R \ln m + R \ln I + S_2. \quad (14)$$

For purposes of later comparison with the formula for polyatomic gases we shall find it convenient to rewrite this equation, introducing symmetrically the two equal moments of inertia I and J , we obtain,

$$S = 7/2R \ln T - R \ln p + 3/2R \ln m + 1/2R \ln I + 1/2R \ln J + S_2. \quad (14a)$$

The Entropy of a Polyatomic Gas.—Consider a polyatomic gas composed of rigid molecules having three moments of inertia I , J and K . Proceeding as above, at temperatures high enough so that the specific heat at constant pressure is exactly $4R$ we may write for the entropy per mol,

$$S = 4R \ln T - R \ln p + \phi(m, I, J, K).$$

If this is a general equation of physics, it must remain invariant when we substitute our transformation equations. We obtain,

$$S' = 4R \ln \frac{I'}{\alpha} - R \ln \frac{p'}{\alpha^4} + \phi\left(\frac{m'}{\alpha}, \alpha I', \alpha J', \alpha K'\right).$$

Making the reasonable assumption that the dependence of entropy on molecular weight m and on the two moments of inertia I and J is the same as shown by Equation 14a for a diatomic gas, it is evident that our desired invariance can only be secured if the function ϕ has the form,

$$\theta(m, I, J, K) = 3/2R \ln m + 1/2R \ln I + 1/2R \ln J + 1/2R \ln K + S_3$$

where S_3 is the same constant for all polyatomic gases. We obtain as our expression for the entropy of our ideal polyatomic gas,

$$S = 4R \ln T - R \ln p + 3/2R \ln m + 1/2R \ln IJ K + S_3. \quad (15)$$

Comparison with the Equations of Sackur, Tetrode, Schames and Latimer.

Sackur, Tetrode and Schames¹ basing their work on various methods of attack which have been suggested by the development of the quantum theory, have all of them derived equations which agree in form with our Equations (13), (14) and (15), for the entropy of monatomic, rigid diatomic, and rigid polyatomic gases. These investigators do not come to complete agreement as to the magnitude of the constants which we have called S_1 , S_2 and S_3 but their equations do agree with ours as to the way entropy depends on temperature, pressure, molecular weight and moments of inertia of the molecules.

Latimer¹ has recently suggested that at a given pressure and temperature, the entropy of a diatomic gas is given by the formula

$$S = 3/2R \ln m + 1/2R \ln a_1 + 1/2R \ln a_2 + C, \quad (16)$$

where m is the molecular weight, a_1 and a_2 are the atomic weights of the two atoms in the molecule and the constant C has a definite value at some one pressure and temperature. This equation does not agree with our Equation (14).

In the next section, where we shall discuss the agreement of our Equation (14) with the experimental facts, it will be shown that the approximate agreement of Latimer's Equation (16) with the data can be explained as due to the small difference in molecular diameters for the gases considered.

Comparison with Experimental Data.

Monatomic Gases.—A comparison of the available experimental data with our Equation (13) for the entropy of monatomic gases has already been made by the author.¹

Diatomic Gases.—In order to compare the predictions of Equation (14) for the entropy of diatomic gases with the experimental data, we shall need an expression for the moment of inertia of diatomic gases in terms of the atomic weights a_1 and a_2 of the two atoms and the molecular diameter σ . This can easily be obtained.

Consider Fig. 1, where c is the center of gravity of the molecule. The moment of inertia I around an axis drawn through c , perpendicular to the line connecting the two atoms, will evidently be,

$$I = a_1 r_1^2 + a_2 r_2^2. \quad (17)$$

Since c is the center of gravity, however, we may write,

$$a_2 r_2 = a_1 r_1 \quad r_2 = \frac{a_1}{a_2} r_1. \quad (18)$$

¹ *Loc. cit.*

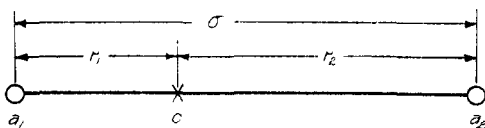


Fig. 1.

We may also write \bar{r} for the molecular diameter,

$$\sigma = r_1 + r_2. \quad (19)$$

Substituting (18) we obtain,

$$\sigma = r_1 \left(1 + \frac{a_1}{a_2} \right),$$

$$r_1 = \frac{a_2}{a_1 + a_2} \sigma = \frac{a_2}{m} \sigma. \quad (20)$$

Similarly,

$$r_2 = \frac{a_1}{a_1 + a_2} \sigma = \frac{a_1}{m} \sigma. \quad (21)$$

Substituting (20) and (21) in (17) and noting that $a_1 + a_2 = m$, we obtain,

$$I = \left(\frac{a_1 a_2^2}{m^2} + \frac{a_2 a_1^2}{m^2} \right) \sigma^2 = \frac{a_1 a_2}{m} \sigma^2, \quad (22)$$

which is the desired expression. Substituting in Equation (14) we obtain for the entropy of perfect rigid diatomic gases at temperatures where the specific heat at constant pressure is exactly $7/2R$,

$$S = 7/2R \ln T - R \ln p + 3/2R \ln m + R \ln \frac{a_1 a_2}{m} \sigma^2 + S_2. \quad (23)$$

For cases where the two atoms are of equal mass $a_1 = a_2$, this may be changed for purposes of comparing with Latimer's equation into the form,

$$S = 3/2R \ln m + 1/2R \ln a_1 + 1/2R \ln a_2 +$$

$$\left(R \ln \frac{\sigma^2}{4} + 7/2R \ln T - R \ln p + S_2 \right).$$

Since molecular diameters σ are about the same for different molecules, it is not surprising that Latimer's equation for $T = 298$, $p = 1$,

$$S = 3/2R \ln m + 1/2R \ln a_1 + 1/2R \ln a_2 + C,$$

as well as our own equation, should both give approximate agreement with the experimental facts for molecules composed of two atoms which have the same or nearly the same atomic weight.

To test Equation (23) we may use the experimental values for the entropy at 298° K. and one atmosphere presented by Latimer¹ and may use as our figures for molecular diameters those of Sutherland,² determined by the best methods provided by the kinetic theory of gases.

At 298° K. and one atmosphere pressure we may include the terms

¹ *Loc. cit.*

² Sutherland, *Phil. Mag.*, 19, 25 (1910).

containing temperature and pressure with our constant and rewrite Equation (23) in the form,

$$S_{298^\circ} = R \ln m^{1/2} a_1 a_2 \sigma^2 + S_2'.$$

Using the available data we have determined the value S_2' , and may rewrite our equation in the form,

$$S_{298^\circ} = 4.573 \log m^{1/2} a_1 a_2 \sigma^2 + 28.26, \quad (24)$$

where S is in calories per degree, m , a_1 and a_2 are in grams per mol and σ is in centimeters times 10^{-8} .

Applying Equation (24) to the only gases for which Sutherland has given values of molecular diameter σ and Latimer of entropy S we obtain the results shown in the following table:

Gas.	σ in cms. $\times 10^{-8}$.	S Experimental.	S Equation 24.	S Latimer.
H ₂	2.17	31.8	32.06	32.30
N ₂	2.95	45.6	46.36	45.42
CO	2.74	45.55	46.03	45.50
O ₂	2.71	48.2	46.68	46.08
Cl ₂	3.76	55.6 (50.0)	51.93	50.04

As far as expressing the experimental facts, there is little to choose between Equation (24) and Latimer's equation.

It is very unfortunate that Sutherland's data on molecular diameter do not include a diatomic gas with atoms having widely different atomic weights, since our Equation (24) and Latimer's show greater differences for such a case. Assuming, however, that the diameter of the hydrogen chloride molecule is the mean of the diameters of the hydrogen and chlorine molecules, Equation (24) gives 43.24 for the entropy of hydrogen chloride, Latimer's equation gives 44.49 and the experimental value is 43.25.

An exact correspondence between the experimental data and Equation (24) is not to be expected, since the derivation of the equation assumes a perfect gas with rigid diatomic molecules in the temperature range where the specific heat at constant pressure is exactly $7/2R$, and these conditions are presumably not exactly true for any actual diatomic gas.

The data on the molecular diameters and entropies of polyatomic gases do not seem suitable for testing Equation (15).

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NOTE.

Modifications of the Adiabatic Calorimeter.—The adiabatic method of calorimetry was introduced in 1905 by T. W. Richards.¹ In 1914,² I constructed a modified adiabatic calorimeter, in connection with my measurements on the heat of combustion of benzoic acid, which it appeared to me was more convenient in use. The heating of

¹ *Proc. Am. Acad.*, **41**, 3 (1905); *Z. physik. Chem.*, **52**, 551 (1905).

² *J. Russ. Phys. Chem. Soc.*, **46**, 935 (1914).