ON THE DEFINITION OF THE IDEAL GAS.

By Edgar Buckingham.

1. *Nature and purpose of the definition.*—The notion of the ideal gas is that of a gas having particularly simple physical properties to which the properties of the real gases may be considered as approximations; or of a standard to which the real gases may be referred, the properties of the ideal gas being simply defined and the properties of the real gases being then expressible as the properties of the standard plus certain corrections which pertain to the individual gases. The smaller these corrections the more nearly the real gas approaches to being in the "ideal state." This conception grew naturally from the fact that the earlier experiments on gases showed that they did not differ much in their physical properties, so that it was possible to define an ideal standard in such a way that the corrections above referred to should in fact all be "small" in terms of the unavoidable errors of experiment. Such a conception would hardly arise to-day, or if it did, would not be so simple as that which has come down to us from earlier times when the art of experimenting upon gases was less advanced.

It is evident that a quantitative definition of the ideal standard gas needs to be more or less complete and precise according to the nature of the problem under immediate consideration. If changes of temperature and of internal energy play no part, all that is usually needed is a standard relation between pressure and volume. Boyle's law is universally adopted as this standard relation, so that the equation

$$(pv)_t = \text{constant} \tag{1}$$

is always a part of the definition of the ideal gas. In problems relating to the behavior of gases at either constant volume or

constant pressure, the p,v relation is sometimes of no importance, so that Boyle's law might be omitted from the definition with no sacrifice of the utility of the standard; but in practice, Boyle's law is always included, either directly or by implication.

Now, two gases might, conceivably, obey Boyle's law within any desired limit of precision and yet differ sensibly in relation to changes of temperature or of internal energy. Hence, if such changes enter into the problem at hand, the properties of our standard or ideal gas need further specification. For many physical purposes one further specification suffices. If, however, we go further and enter upon the consideration of chemical reactions, the properties of the standard may, with advantage, be still further specified.

2. *Absolute temperature.*—The absolute temperature by a gas thermometer is defined, on the constant pressure scale, by the equation

$$T_p = \text{const} \times v \tag{2}$$

or, on the constant volume scale, by the equation

$$T_v = \text{const} \times p \tag{3}$$

If the gas obeys Boyle's law, these two independent scales become identical,[1] if the size of the degree is the same for both, as, for instance, when the ice and steam points are made 100° apart on both scales. Hence we have the equation

$$pv = \text{const} \times T \tag{4}$$

as the definition of *the* absolute temperature on the scale of a thermometer filled with a gas that follows Boyle's law.

The thermodynamic temperature θ which constantly appears in the equations of thermodynamics is defined in quite another way. By Carnot's theorem the efficiency, E, of any thermal engine working periodically and reversibly by taking in heat from a hot body and giving out heat to a cold body, is the same for all such engines and depends only on the temperatures of the hot and cold bodies. By the principle of the equivalence of work and heat, the work W done by the engine during one cycle is equivalent

[1] See Note I at the end of this paper.

to the excess of the heat Q_1 taken in from the hot body over the heat Q_2 given out to the cold body, so that we must have

$$E = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \tag{5}$$

Carnot's theorem makes no reference to the numerical values by which the temperatures of the two bodies may happen to be designated, nor even to the possibility of numbering temperatures at all; it does not involve the conception of temperature as a measurable quantity. Nevertheless, Carnot's theorem furnishes us with a convenient and simple scheme for numbering temperatures.

Let equation (5) be put in the form

$$\frac{Q_1}{Q_2} = \frac{1}{1 - E} \tag{6}$$

Then, since E depends only on the two temperatures, the same is true of Q_1/Q_2, so that for any two temperatures Carnot's theorem determines a number—the value of this ratio Q_1/Q_2. Now, since it is convenient in reasoning about temperatures to have the temperatures numbered, for identification, in accordance with some system, i. e., with some "thermometric scale," and since we are at liberty to select whatever system we find convenient, let us assign to any two temperatures such numbers θ_1 and θ_2 as shall have the same ratio as Q_1 and Q_2, θ_1 being the higher of the two temperatures. We then have the equation

$$\frac{\theta_1}{\theta_2} = \frac{Q_1}{Q_2} \tag{6}$$

as one element in the definition of a scale of temperature. The definition may be completed and the numerical value of every temperature fixed, by specifying that the numbers pertaining to the ice and steam points shall differ by 100, as in the common centigrade scales.

This system of numbering temperatures was devised by Kelvin in 1854 and is known as Kelvin's scale or the thermodynamic absolute scale. It may be simply defined, except as to size of the

degree, by saying: Any two temperatures are to each other as the quantities of heat taken in and given out at these temperatures by a reversible thermal engine working between them, i. e., with its source at the higher and its refrigerator at the lower.

Carnot's theorem may then be put in the convenient and familiar form

$$E=\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1} \tag{7}$$

the general form being

$$E=\frac{Q_1-Q_2}{Q_1}=f\ (t_1,\ t_2) \tag{8}$$

when the scale of temperature, t, has not yet been specified.

Suppose, now, that we imagine the cylinder of the Carnot engine to be filled with a substance of which the mechanical and thermal properties are well known; it may be possible to find from these properties the value of W/Q_1 or E, in terms of the scale of temperature t, in which these properties are expressed. Since all reversible engines have the same efficiency, the value of E thus found will give us the value of $f\ (t_1, t_2)$ in equation (8) and so furnish a relation between t_1 and t_2 on the one hand, and θ_1 and θ_2 on the other, through the intermediation of equation (7). Suppose, in particular, that the cylinder of the engine is filled with a gas that follows Boyle's law so that we may use equation (4). When we try to find the value of W/Q_1 by using equation (4), it turns out that the problem can be solved if, and only if, we assume that the heat taken in during an isothermal expansion is all converted into outside work, or, in other words, that the internal energy of the gas does not change. The very simple result is, in this case,

$$\frac{W}{Q_1}=\frac{Q_1-Q_2}{Q_1}=\frac{T_1-T_2}{T_1} \tag{9}$$

or

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2} \tag{10}$$

The proof of this proposition is given in all text-books of thermodynamics and need not be repeated here.

We see, then, that if a thermometer is filled with a gas which (*a*) obeys Boyle's law, and (*b*) suffers no change of internal energy during change of volume at constant temperature, the ratio T_1/T_2 of any two temperatures measured on this thermometer is the same as the ratio Q_1/Q_2 of the quantities of heat taken in and given out by a reversible engine working between these temperatures. And since by definition θ_1/θ_2 is equal to this same ratio, it follows that.

$$\frac{T_1}{T_2}=\frac{\theta_1}{\theta_2} \tag{11}$$

and the two scales are proportional and may be made identical by proper choice of the degrees. For such a gas we therefore have

$$T=\text{const}\times\theta \tag{12}$$

and equation (4) may be written in the form

$$pv=R\theta \tag{13}$$

R being a constant depending on the mass of gas and the units of p, v, θ.

In quantitative reasoning about gases, the absolute temperatures T_p and T_v occur very frequently. But in all thermodynamic equations, Kelvin's thermodynamic absolute temperature θ is also continually appearing. Our work is therefore much simplified if these three numerical values for any given temperature are identical, so that a single symbol for temperature is enough. The two gas-scale temperatures, T_p and T_v, become identical if the gas obeys Boyle's law; and, as has just been said, their common value T becomes, with the proper choice of degrees, identical with θ, if in addition, the internal energy of the gas is independent of the volume at constant temperature, i. e., if

$$\left(\frac{\partial\epsilon}{\partial v}\right)_\theta=0 \tag{14}$$

Evidently, therefore, it is highly desirable that our ideal standard shall be so defined as to insure the validity of equation (13), if this can be done without making the ideal gas differ too much from the real gases. We have, then, to consider whether $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$ is nearly zero for the real gases. If it is, equation (14) may be made a part of the definition of the ideal gas and the properties of the real gases still be regarded as differing from those of the ideal standard by quantities small enough to be considered as mere correction terms and disregarded in a first approximation.

3. *The Gay-Lussac effect.*—If we let a gas expand "freely," i. e., without doing any outside work, any change of its internal energy must be compensated by a gain or loss of heat. And, conversely, any gain or loss of heat involves a corresponding change of the internal energy. Suppose that the process is made isothermal; then unless equation (14) is satisfied there will be an absorption or development of heat. If, on the other hand, the expansion is so sudden as to be nearly adiabatic, the temperature of the gas will fall, if the isothermal process required the addition of heat and rise in the opposite case. Hence, if in a sudden free expansion the mean temperature of the gas neither rises nor falls, there has been no tendency to take in or give out heat, and the internal energy has therefore not changed. Hence equation (14) is satisfied for this gas within the limits of observational error of the method.

In 1807 Gay-Lussac published the results of experiments of this sort on air, hydrogen, carbonic acid, and oxygen. He found that when the gas expanded by rushing from one vessel into another of the same size, previously exhausted, its mean temperature did not change by an amount which he could detect with certainty, the temperature in the first vessel falling as much as that in the second rose. Later experiments of a somewhat similar nature by Joule gave a like result. We may therefore conclude that for these gases the quantity $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$, or the "Gay-Lussac effect," is small and equation (14) nearly satisfied. Hence, if we make it a part of our definition of the ideal gas that equation (14) shall be exactly satisfied, or that the Gay-Lussac effect shall be exactly

zero, the gas thus defined will fulfill the requirement of representing the real gases with errors small enough to be negligible in a first approximation. The statement that the internal energy of a gas is independent of the volume during isothermal changes, which has here been put more briefly in the statement that the Gay-Lussac effect is zero, is commonly known as Joule's law.

Our results so far may then be shortly stated as follows: If a gas obeys Boyle's law, its constant pressure and constant volume scales agree; and if, in addition, it obeys Joule's law, its scale agrees with Kelvin's scale. In other words, equations (1) and (14) suffice for the validity of equation (13); and furthermore, equations (1) and (14) are nearly enough fulfilled by the ordinary real gases under ordinary conditions that they are suitable elements in the mathematical definition of the properties of an ideal standard gas for which we may then consider equation (13) as satisfied, this equation being of the highest utility in thermodynamic reasoning.

Having shown that equations (1) and (14) lead to equation (13), it is well also to show that they may be deduced from it or that (1) and (14) taken together are in all respects equivalent to (13). It is at once evident, if θ is set constant, that a gas which satisfies equation (13) must obey Boyle's law, so that we need only consider the Gay-Lussac effect, for which we shall deduce a general equation.

If ϵ represents the internal energy of any body, Q heat added to it, and W work done on it, the first law of thermodynamics states that in any infinitesimal change of state

$$\delta\epsilon = \delta Q + \delta W \tag{15}$$

The second law, in one of its various forms, states that if the change is reversible, $\delta Q/\theta$ is a complete differential, and that we may therefore write, for a reversible change,

$$\delta Q = \theta\delta\eta \tag{16}$$

where η, known as the entropy, is the quantity, completely determined by the state of the body, of which $\delta Q/\theta$ is the differential. If the only outside force on the body is a uniform normal pressure on its surface, the work done on the body may be written

$$\delta W = -p\delta v \tag{17}$$

Hence, for any such change of state, the two laws of thermodynamics may be summarized in the equation

$$\delta\epsilon = \theta\delta\eta - p\delta v \tag{18}$$

If the change is isothermal, this gives us

$$\left(\frac{\partial\epsilon}{\partial v}\right)_\theta = \theta\left(\frac{\partial\eta}{\partial v}\right)_\theta - p \tag{19}$$

Subtracting $\delta(\theta\eta)$ from both members of (18) we have

$$\delta(\epsilon - \theta\eta) = -\eta\delta\theta - p\delta v \tag{20}$$

and since changes of energy and entropy can occur only when the state of the body changes, $(\epsilon - \theta\eta)$ must be treated as a function of θ and v only, and the second member of equation (20) is a complete differential. It follows that

$$\left(\frac{\partial\eta}{\partial v}\right)_\theta = \left(\frac{\partial p}{\partial\theta}\right)_v \tag{21}$$

so that (19) may be put in the more intelligible form

$$\left(\frac{\partial\epsilon}{\partial v}\right)_\theta = \theta\left(\frac{\partial p}{\partial\theta}\right)_v - p \tag{22}$$

This perfectly general expression for the Gay-Lussac effect in any fluid was given in sensibly this form by Kelvin[2] in 1851.

From equation (22) we can compute the value of the Gay-Lussac effect for any fluid for which we know the p,θ relation. In particular, let the fluid be a gas which satisfies equation (13). We have at once, by differentiation and substitution in equation (22),

$$\left(\frac{\partial\epsilon}{\partial v}\right)_\theta = \theta\frac{R}{v} - p = 0 \tag{23}$$

so that equation (14) is necessary as well as, with (1), sufficient for the validity of (13). It is evident, however, that (14) may be satisfied by a substance that does not obey Boyle's law. It is

[2] Math. Phys. Papers **1**, p. 227, equ. (4′)

merely necessary that the constant volume scale of the given gas agree with the thermodynamic scale or that

$$p = A\theta \quad (v \text{ constant}) \tag{24}$$

for by differentiating and substituting in (22) we have

$$\left(\frac{\partial \epsilon}{\partial v}\right)_\theta = \theta A - p = 0 \tag{25}$$

And furthermore, setting the second member of (22) equal to zero and integrating at constant volume leads directly to (24). Hence, if any gas obeys Joule's law, its constant volume scale agrees with Kelvin's scale, and vice versa, regardless of whether Boyle's law is satisfied. Evidently, then, for some purposes, in problems not concerned with changes in volume, a gas that obeys Joule's law exactly is sufficient as a standard and might be taken, in dealing with such problems, as the ideal gas.

4. *The usual definition of the ideal gas.*—The ideal gas is, then, usually defined as follows:

(*a*) It obeys Boyle's law; and either

(*b*) Its temperature scale agrees with the thermodynamic scale, or

(*b'*) It obeys Joule's law, i. e., its Gay-Lussac effect is zero.

We have shown that these two definitions are equivalent in all respects, *b'* following from *a* and *b*, and *b* from *a* and *b'*. It may, however, be remarked that from an experimental standpoint neither *b* nor *b'* is altogether satisfactory. For it is desirable to have the ideal standard defined in terms of quantities that are easily accessible to experiment, so that any real gas may easily be tested to find how far it comes short of being in the ideal state. The statement of Boyle's law is perfectly satisfactory in this regard. But since we have no thermometer which reads directly in terms of the thermodynamic scale, we have no easy means of finding how the scale of any given gas thermometer deviates from that scale. The alternative specification that the ideal gas satisfies Joule's law suffers under a like disability. The Gay-Lussac experiment, or Joule's modification of it, is difficult or

impossible to carry out with the desired accuracy, as is shown by the fact that so able an experimenter as Joule got only negative results, although we are certain that the Gay-Lussac effect is not generally zero for any of the real gases.

The above definition of the ideal gas is therefore practically somewhat defective, though mathematically satisfactory, and we may ask whether the second part of the definition, b or b', can not be so changed as to have a closer relation to practicable experimental work. The answer to this question was given by Kelvin[3] in 1851, when, after the above-mentioned experiments of Joule, he invented the famous porous-plug experiment as a substitute for the free-expansion experiments.

5. *The Joule-Kelvin effect.*—Let the gas to be studied be forced uniformly, and so slowly that its kinetic energy is negligible, through a pipe which is stopped at one point by a plug of porous material. If the plug is sufficiently fine grained, the gas issues from it uniformly and quietly at a pressure somewhat lower than that at which it entered the plug. During the change of state of a given mass of gas which consists in passing through the plug from the higher to the lower pressure, the following equation must be fulfilled:

Heat put in = increase of energy + work given out.

The work done on 1 gram of gas, while it is entering the plug, by the gas behind it, is evidently the product of its specific volume and the constant pressure to which it is subject, or pv. As the gas issues from the plug, the work it does on the gas ahead of it is, similarly, the product of the new specific volume by the constant lower pressure. The whole work given out by the gram of gas is therefore the difference of these or the increase in the value of the product pv. Hence if the drop of pressure in the plug is infinitesimal we have

$$\delta Q = \delta\epsilon + \delta(pv) \tag{26}$$

[3] 3 Math. Phys. Papers, **1**, p. 220.

or, if δp is the numerical value of the drop in pressure,

$$\frac{\delta Q}{\delta p}=\frac{\delta \epsilon}{\delta p}+\frac{\delta(pv)}{\delta p} \tag{27}$$

We have as yet said nothing about possible changes of temperature, and equations (26) and (27) are quite general, being merely expressions of the first law as applied to this particular sort of change of state.

Let us now specialize by assuming the rate of supply or withdrawal of heat to be such as to prevent the gas from changing in temperature as it flows through the plug; then equation (27) reduces to

$$\left(\frac{\partial Q}{\partial p}\right)_\theta=\left(\frac{\partial \epsilon}{\partial p}\right)_\theta+\frac{\partial}{\partial p}(pv)_\theta \tag{28}$$

Let the heat supplied to unit mass of gas per unit *fall* of pressure be denoted by ρ, so that $\delta Q=\rho\ (-\delta p)$ or

$$\rho=-\left(\frac{\partial Q}{\partial p}\right)_\theta \tag{29}$$

The quantity ρ is known as the "Joule-Thomson or Joule-Kelvin effect." Equation (28) may now be written

$$\rho=-\left(\frac{\partial \epsilon}{\partial p}\right)_\theta-\frac{\partial}{\partial p}(pv)_\theta \tag{30}$$

which is merely a mathematical way of saying that as the gas flows through the plug the rate of absorption of heat equals the rate of increase of internal energy plus the rate of doing outside work.

Returning now to our former definition of the ideal gas, we see that if Boyle's law holds, the last term of equation (30) vanishes, leaving

$$\rho=-\left(\frac{\partial \epsilon}{\partial p}\right)_\theta \tag{31}$$

But we have

$$\left(\frac{\partial \epsilon}{\partial p}\right)_\theta=\left(\frac{\partial \epsilon}{\partial v}\right)_\theta\left(\frac{\partial v}{\partial p}\right)_\theta \tag{32}$$

and since $\left(\frac{\partial v}{\partial p}\right)_\theta$ could vanish only for an absolutely incompressible substance, it follows that $\left(\frac{\partial \epsilon}{\partial p}\right)_\theta$ and $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$ must vanish together, if at all. Hence, for a gas that obeys Boyle's law and therefore satisfies equation (31) it is indifferent whether we specify that the Gay-Lussac effect shall vanish or that the Joule-Kelvin effect shall do so, and the second specification of our former definition may be replaced by this new one, if this is otherwise satisfactory as a part of the definition. It is satisfactory; for the Joule-Kelvin effect may be measured more accurately than the Gay-Lussac effect, and is therefore, from a purely physical point of view, a better quantity than the Gay-Lussac effect to have appearing in the equations which embody the definition. Furthermore, though measurable, it is small for the ordinary gases under ordinary conditions; so that if the ideal gas satisfies the condition of showing no Joule-Kelvin effect, it still fulfills the requirement of not differing much from the real gases. We may then adopt the equation

$$\rho = 0 \tag{33}$$

as substitute for (14), when taken together with equation (1), in specifying the definition of an ideal gas which shall satisfy equation (13).

It is sometimes implied that expansion through a porous plug is equivalent to a free expansion.[4] If the gas is one that obeys Boyle's law, this is true for an isothermal expansion, since pv does not change and no external work is done. But unless Boyle's law holds this is not the case, and a gas that showed no Gay-Lussac effect might still show a Joule-Kelvin effect. For though by equation (32) the term $\left(\frac{\partial \epsilon}{\partial p}\right)_\theta$ of equation (30) vanishes if the gas obeys Joule's law, equation (33) will not be satisfied unless the gas obeys Boyle's law. Hence, the specification that the gas shall

[4] See Note II at the end of this paper.

show no Joule-Kelvin effect can not replace the specification that it shall obey Joule's law unless it is also specified that the gas shall obey Boyle's law.

It is well to show directly that equation (33) follows from equation (13) by deducing a general equation for the Joule-Kelvin effect as we did in section 3 for the Gay-Lussac effect. Let us write equation (30) in the form

$$\rho = -\left(\frac{\partial \epsilon}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial p}\right)_\theta - p\left(\frac{\partial v}{\partial p}\right)_\theta - v \tag{34}$$

By taking the value of $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$ from equation (22), and utilizing the the relation [5]

$$\left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v \left(\frac{\partial \theta}{\partial v}\right)_p = -1 \tag{35}$$

equation (34) may at once be reduced to the form

$$\rho = \theta\left(\frac{\partial v}{\partial \theta}\right)_p - v \tag{36}$$

Like equation (22) for the Gay-Lussac effect, this equation is general and applies to any fluid. From it we may compute the value of ρ for any substance for which the v,θ relation is known. In particular, if the substance is a gas which satisfies equation (13), differentiation and substitution in (36) give us

$$\rho = \theta\frac{R}{p} - v = 0 \tag{37}$$

so that the Joule-Kelvin effect is zero if the gas is ideal by the definition contained in equation (13).

Since the p,v relation is not involved in equation (36), we may have $\rho = 0$ for a gas which does not obey Boyle's law. In fact, if we set the second member of (36) equal to zero and integrate at constant pressure, we get

$$v = B\theta \qquad (p \text{ constant}) \tag{38}$$

[5] See Note I at the end of this paper.

Hence, in order that the Joule-Kelvin effect shall vanish, it is necessary and sufficient that the constant-pressure scale of the gas in question shall agree with the thermodynamic scale and the gas need not obey Boyle's law.

As regards insuring the validity of equation (13), we might dispense with any explicit reference to Boyle's law and merely say that the Gay-Lussac and Joule-Kelvin effects shall both be zero. For if, in equation (30), ρ is zero; and if in addition $\left(\frac{\partial \epsilon}{\partial p}\right)_\theta$ is zero, as it is by equation (32) when the Gay-Lussac effect is zero, it follows that $\frac{\partial}{\partial p}(pv)_\theta$ is also zero, or that Boyle's law is fulfilled. Since, however, Boyle's law is the simplest part of the definition of our ideal standard gas, it would, in general, be disadvantageous to replace it by something else that is less simple.

6. *The specific heats.*—For many purposes the definition of the standard or ideal gas as already given is sufficient. Whenever in comparing the behavior of different gases we find some property which is nearly the same for all, it may be convenient, as a first approximation, to treat this property as exactly the same for all, so that reasoning about it shall apply to all the gases indifferently. We may, in other words, assign some fixed average value of this property to the ideal gas, to which the real gases are then approximations. The notion of the ideal gas might thus evidently be greatly enlarged and its definition extended to include a large number of specifications. There is no logical reason for stopping at one point rather than another; but in practice, the definition is usually terminated at the point already reached, the only further extension that is at all common being a statement regarding the specific heats.

During a change of temperature at constant volume no outside work is done, so that any heat taken in goes to increasing the internal energy, and we have the equation

$$C_v = \left(\frac{\partial \epsilon}{\partial \theta}\right)_v \tag{39}$$

as one way of defining the specific heat at constant volume. By differentiating with regard to v and noting that since v and θ are independent, the order or differentiation may be inverted, we get

$$\left(\frac{\partial C_v}{\partial v}\right)_\theta = \left[\frac{\partial}{\partial v}\left(\frac{\partial \epsilon}{\partial \theta}\right)_v\right]_\theta = \left[\frac{\partial}{\partial \theta}\left(\frac{\partial \epsilon}{\partial v}\right)_\theta\right]_v \tag{40}$$

Hence, if the Gay-Lussac effect $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$ is zero, as for the ideal gas already defined, it follows that $\left(\frac{\partial C_v}{\partial v}\right)_\theta = 0$, and the specific heat at constant volume does not change with the volume so long as the temperature is constant. Experiment shows that for the real gases under ordinary conditions C_v is nearly constant. Hence, it is frequently made a part of the definition of the ideal gas that C_v shall be exactly constant. As we have just seen, C_v must be independent of the volume for the ideal gas already defined, but the statement that it shall also be independent of the temperature can not be deduced from the former definition and constitutes a new and independent element in the definition.

It is easily shown that for a gas that satisfies equation (13) the specific heats at constant volume and at constant pressure differ only by an absolute constant. Hence, from a mathematical standpoint it is immaterial whether we make the new addition to our definition by saying that C_v shall be constant or that C_p shall be constant; the former is more usual. There is, however, a difference in one respect, namely, that for the real gases the variations of C_v with temperature are much smaller than those of C_p, thus making the specification

$$\left(\frac{\partial C_v}{\partial \theta}\right)_v = 0 \tag{41}$$

the best form in which to put the addition to our old definition, as it is the most usual.

7. *Recapitulation of the definition.*—We find in common use the following definitions of the ideal gas which we have shown to be in all respects mutually equivalent, each being necessary and sufficient for the others:

(*A*) The ideal gas obeys Boyle's law and its temperature scale agrees with the thermodynamic scale; i. e.:

$$(pv)_\theta = \text{const}; \qquad T = \text{const} \times \theta$$

or

$$pv = R\theta$$

(*B*) The ideal gas obeys Boyle's law and Joule's law, i. e.:

$$(pv)_\theta = \text{const}; \qquad \left(\frac{\partial \epsilon}{\partial v}\right)_\theta = \theta\left(\frac{\partial p}{\partial \theta}\right)_v - p = 0$$

(*C*) The ideal gas obeys Boyle's law and its Joule-Kelvin effect is zero, i. e.:

$$(pv)_\theta = \text{const}; \qquad \rho = \theta\left(\frac{\partial v}{\partial \theta}\right)_p - v = 0$$

To these there is frequently added the further independent statement that:

(*D*) The specific heat of the ideal gas at constant volume is independent of the temperature, i. e.:

$$\left(\frac{\partial C_v}{\partial \theta}\right)_v = 0$$

Many further additions to the definition might be, but in ordinary practice are not, made.

The equations of thermodynamics may, by mere mathematical transformation and without the introduction of new physical facts, be put into such a vast array of different forms that the same substance may often be expressed in a variety of different ways in either words or equations. For some purposes the above definition might be expressed more conveniently in other sets of equations or in other statements about physical properties; but the form of definition given under (*A*), (*B*), or (*C*), with or without the addition of (*D*), contains the substance of the notion of the ideal standard gas as that notion is most generally used, and the equations are convenient mathematical expressions of it.

8. *The cohesion pressure of a real gas.*—If a gas has any self-attraction or cohesion, expansion involves an increase of the potential

energy of the attraction by an amount equal to the work done against the attractive forces. In an isothermal expansion, this forms a part of the value of $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$, but it need not form the whole. From the molecular-kinetic point of view, on which the mean kinetic energy of molecular translation is determined solely by the temperature, an increase of internal energy during isothermal expansion goes in part to increasing the intermolecular potential energy, but it may also, in any but a simple monatomic gas, go in part to increasing interatomic intramolecular potential energy if, as is quite conceivable, the molecules change their forms or dimensions with changing mean distance of separation and changing frequency of collision. If by cohesion we mean the attraction between the molecules, which acts to retard any molecule approaching the bounding surface of the gas and so decreases the mean change of momentum upon reflection, and therefore the pressure on the bounding wall, then we must admit that an absence of cohesion does not suffice to insure that the internal energy shall not change during an isothermal expansion. Or if by the "cohesion pressure" we mean the extra pressure that would have to be applied from without to preserve the same volume if the intermolecular attractions could be annihilated without otherwise changing the nature of the gas, then saying that the cohesion pressure is zero is not equivalent to saying that the Gay-Lussac effect is zero or that the gas obeys Joule's law. To put this idea in more precise form we may proceed somewhat as follows:

Let π represent the cohesion pressure. Then the equation of state of any fluid may always be written in the form

$$(p+\pi)(v-b)=R\theta \tag{42}$$

where R is a constant. It must be supposed that in general the intermolecular attractions will depend on both temperature and density, i. e., π will be a function of θ and v. But whatever be the form of π, the remaining quantity b, known as the covolume, may always be adjusted so that the equation shall be satisfied. In general, b also will evidently be a function of θ and v.

From equation (42) we have

$$p = \frac{R\theta}{v-b} - \pi \tag{43}$$

$$\left(\frac{\partial p}{\partial \theta}\right)_v = \frac{R}{v-b} + \frac{R\theta}{(v-b)^2}\left(\frac{\partial b}{\partial \theta}\right)_v - \left(\frac{\partial \pi}{\partial \theta}\right)_v \tag{44}$$

whence by substituting in equation (22) we have, as an expression for the Gay-Lussac effect in terms of π and b

$$\left(\frac{\partial \epsilon}{\partial v}\right)_\theta = \pi - \theta\left(\frac{\partial \pi}{\partial \theta}\right)_v + \frac{R\theta^2}{(v-b)^2}\left(\frac{\partial b}{\partial \theta}\right)_v \tag{45}$$

From this we see that in any isothermal expansion δv, the increase of internal energy $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta \delta v$ is equal to the work $\pi \delta v$ done against the cohesion pressure, plus two other terms which can not in general be set equal to zero. So far as the mathematical form of the equation is concerned, either π or b may be given any expression we please, made constant for example, and the other may still be so adjusted that equation (42) shall represent the behavior of the gas. But in general the last two terms of (45) will not *both* vanish, nor need their sum vanish.

To illustrate, suppose that the equation of state has the simple form given by van der Waals, namely,

$$\left(p + \frac{a}{v^2}\right)(v-b) = R\theta \tag{46}$$

with a, b, and R constant. The derivatives of π and b with regard to θ vanish, and we do have

$$\left(\frac{\partial \epsilon}{\partial v}\right)_\theta = \frac{a}{v^2} = \pi \tag{47}$$

But if we take an equation only slightly more complicated, such as the first equation of Clausius, or

$$\left[p + \frac{a}{\theta(v+c)^2}\right](v-b) = R\theta \tag{48}$$

with a, b, c, and R constant, equation (45) gives us

$$\left(\frac{\partial \epsilon}{\partial v}\right)_\theta = \frac{2a}{\theta(v+c)^2} = 2\pi \tag{49}$$

and only half the Gay-Lussac effect is to be attributed to work done against forces represented by $\pi = \frac{a}{\theta(v+c)^2}$. In more complicated equations, with the covolume dependent on the temperature, the last term of (45) may also have a finite value. The physical interpretation of these two terms is impossible until we have some clear physical reason for assigning a particular mathematical form, $\pi = f(v,\theta)$, to the cohesion pressure π. But it is evident that we can not, offhand, say that the Gay-Lussac effect is a measure of the cohesion; and we can not, in the definition of the ideal gas, replace the specification that it shall obey Joule's law by the specification that its cohesion pressure shall vanish unless we *define* the cohesion pressure as in this case equal to the Gay-Lussac effect, and so to zero. The cohesion pressure is, in the nature of things, not accessible to direct measurement, whereas the Gay-Lussac effect may, in principle at least, be determined by simple experiment. Hence it is, in itself, altogether proper to adopt the equation

$$\left(\frac{\partial \epsilon}{\partial v}\right)_\theta = \pi \tag{50}$$

as a definition of the cohesion pressure.[6] But if we do this we meet another difficulty, for we find that the π thus defined will not fit into equation (42), which is a very useful equation. For since $\left(\frac{\partial \epsilon}{\partial v}\right)_\theta$ is a definite physical property of the gas, equation (50) fixes the form which π must have. But if (50) is to be satisfied and the π so defined is to be identical with the π of the equation (42), equation (45) gives us

$$\left(\frac{\partial \pi}{\partial \theta}\right)_v = \frac{R\theta}{(v-b)^2}\left(\frac{\partial b}{\partial \theta}\right)_v \tag{51}$$

[6] See Webster and Rosanoff, Phys. Rev., Sept., 1909.

And if π is already fixed by equation (50), equation (51) imposes a restriction on b, which can then no longer be adjusted at pleasure, so that, with the value of π already fixed by (50), equation (42) shall represent the behavior of the gas. In other words, the π of equation (50) can not *in general* be identified with the π of equation (42), and the cohesion pressure defined by (50) is not the same as what is usually meant by the cohesion pressure, the usual meaning of the term being that of the π in equation (42).

NOTE I.

(*A*) Let x, y, and z be any three quantities connected by a single relation which permits us to express any one in terms of the other two by an equation of the form

$$z = f\ (x,\ y)$$

Differentiating this we have

$$\delta z = \left(\frac{\partial z}{\partial x}\right)_y \delta x + \left(\frac{\partial z}{\partial y}\right)_x \delta y \tag{a}$$

Now let z be constant, i. e., $\delta z = 0$. This is an added condition, so that x and y can no longer change independently, and we must have

$$\delta x = \left(\frac{\partial x}{\partial y}\right)_z \delta y$$

Introducing this value together with $\delta z = 0$ into equation (a) we have

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \cdot \left(\frac{\partial x}{\partial y}\right)_z \delta y + \left(\frac{\partial z}{\partial y}\right)_x \delta y$$

Dividing by $\left(\frac{\partial z}{\partial y}\right)_x \delta y$ and rearranging, we get this into the more compact form

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1$$

a relation which must always hold between the derivatives of any three quantities of which any two determine the third.

(*B*) Let the three quantities be p, v, and t. Then we have

$$\left(\frac{\partial p}{\partial v}\right)_t \cdot \left(\frac{\partial v}{\partial t}\right)_p \cdot \left(\frac{\partial t}{\partial p}\right)_v = -1 \tag{b}$$

an equation which is frequently useful in transforming thermodynamic equations relating to fluids.

Let the substance considered be a gas that obeys Boyle's law so that

$$(pv)_t = A = f(t) \tag{c}$$

Then we have

$$p = \frac{A}{v} \qquad \left(\frac{\partial p}{\partial v}\right) = -\frac{A}{v^2} = -\frac{p}{v}$$

Substituting in equation (b) and changing signs, we have

$$\frac{p}{v} \cdot \left(\frac{\partial v}{\partial t}\right)_p \cdot \left(\frac{\partial t}{\partial p}\right)_v = 1$$

Dividing this by $p\left(\frac{\partial t}{\partial p}\right)_v$, we have finally

$$\frac{1}{v}\left(\frac{\partial v}{\partial t}\right)_p = \frac{1}{p}\left(\frac{\partial p}{\partial t}\right)_v \tag{d}$$

This equation is merely a statement that as the temperature t (measured on any scale whatever) changes, the fractional change of volume at constant pressure is the same as the fractional change of pressure at constant volume; or that the volume and pressure coefficients are equal.

If we define two separate and independent scales of temperature by a thermometer filled with a gas, one of them T_p proportional to volume at constant pressure, and the other T_v proportional to pressure at constant volume, the two scales must evidently become proportional to each other if the volume and the pressure coefficients are equal, and identical if the degrees are made equal. Hence, for a gas which obeys Boyle's law the T_p and T_v scales agree.

NOTE II.

In Gay-Lussac's free expansion experiments, work was done by the part of the gas that finally remained in the original vessel on the rest of the gas, which passed over into the second vessel; but no work was done on anything outside. During the rush of gas which followed the opening of the stopcock between the two vessels some kinetic energy was produced, but this was soon dissipated by viscosity and the mean temperature of the gas was found to be unchanged, the temperature in the first vessel having fallen as much as that in the second vessel had risen.

In isothermal expansion through a porous plug by a gas that obeys Boyle's law, the phenomena are simpler. As in the Gay-Lussac experiment, no external work is done by the gas since pv does not change. But in addition to this, no one part of the gas does or has done on it more work than another, since the flow is steady and continuous. Furthermore, no sensible kinetic energy is generated, if the plug is sufficiently fine-grained, the dissipation corresponding to that of the eddy currents in Gay-Lussac's experiment taking place in the plug itself and during the expansion, whereas in Gay-Lussac's experiment the dissipation was, in part at all events, subsequent to the expansion. Hence, for a gas that obeys Boyle's law the Joule-Kelvin experiment, when performed isothermally, is equivalent to but somewhat simpler than the Gay-Lussac experiment.

WASHINGTON, November 13, 1909.