

B and C also denoting functions of the temperature. Therefore

$$\mu_1 = B + C \log \frac{m_1^{(L)}}{Av^{(L)}}. \quad (296)$$

It will be seen (if we disregard the difference of notation) that this equation is equivalent in form to (216), which was deduced from *a priori* considerations as a probable relation between the quantity and the potential of a small component. When a liquid absorbs several gases at once, there will be several equations of the form of (296), which will hold true simultaneously, and which we may regard as equivalent to equations (217), (218). The quantities A and C in (216), with the corresponding quantities in (217), (218), were regarded as functions of the temperature and pressure, but since the potentials in liquids are but little affected by the pressure, we might anticipate that these quantities in the case of liquids might be regarded as functions of the temperature alone.

In regard to equations (216), (217), (218), we may now observe that by (264) and (276) they are shown to hold true in ideal gases or gas-mixtures, not only for components which form only a small part of the whole gas-mixture, but without any such limitation, and not only approximately but absolutely. It is noticeable that in this case quantities A and C are functions of the temperature alone, and do not even depend upon the nature of the gaseous mass, except upon the particular component to which they relate. As all gaseous bodies are generally supposed to approximate to the laws of ideal gases when sufficiently rarefied, we may regard these equations as approximately valid for gaseous bodies in general when the density is sufficiently small. When the density of the gaseous mass is very great, but the separate density of the component in question is small, the equations will probably hold true, but the values of A and C may not be entirely independent of the pressure, or of the composition of the mass in respect to its principal components. These equations will also apply, as we have just seen, to the potentials in liquid bodies for components of which the density in the liquid is very small, whenever these components exist also in the gaseous state, and conform to the law of Henry. This seems to indicate that the law expressed by these equations has a very general application.

*Considerations relating to the Increase of Entropy due to the
Mixture of Gases by Diffusion.*

From equations (278) we may easily calculate the increase of entropy which takes place when two different gases are mixed by diffusion, at a constant temperature and pressure. Let us suppose

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that the quantities of the gases are such that each occupies initially one half of the total volume. If we denote this volume by V , the increase of entropy will be

$$m_1 a_1 \log V + m_2 a_2 \log V - m_1 a_1 \log \frac{V}{2} - m_2 a_2 \log \frac{V}{2},$$

or

$$(m_1 a_1 + m_2 a_2) \log 2.$$

Now

$$m_1 a_1 = \frac{pV}{2t}, \quad \text{and} \quad m_2 a_2 = \frac{pV}{2t}.$$

Therefore the increase of entropy may be represented by the expression

$$\frac{pV}{t} \log 2. \quad (297)$$

It is noticeable that the value of this expression does not depend upon the kinds of gas which are concerned, if the quantities are such as has been supposed, except that the gases which are mixed must be of different kinds. If we should bring into contact two masses of the same kind of gas, they would also mix, but there would be no increase of entropy. But in regard to the relation which this case bears to the preceding, we must bear in mind the following considerations. When we say that when two different gases mix by diffusion, as we have supposed, the energy of the whole remains constant, and the entropy receives a certain increase, we mean that the gases could be separated and brought to the same volume and temperature which they had at first by means of certain changes in external bodies, for example, by the passage of a certain amount of heat from a warmer to a colder body. But when we say that when two gas-masses of the same kind are mixed under similar circumstances there is no change of energy or entropy, we do not mean that the gases which have been mixed can be separated without change to external bodies. On the contrary, the separation of the gases is entirely impossible. We call the energy and entropy of the gas-masses when mixed the same as when they were unmixed, because we do not recognize any difference in the substance of the two masses. So when gases of different kinds are mixed, if we ask what changes in external bodies are necessary to bring the system to its original state, we do not mean a state in which each particle shall occupy more or less exactly the same position as at some previous epoch, but only a state which shall be undistinguishable from the previous one in its sensible properties. It is to states of systems thus incompletely defined that the problems of thermodynamics relate.

But if such considerations explain why the mixture of gas-masses

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of the same kind stands on a different footing from the mixture of gas-masses of different kinds, the fact is not less significant that the increase of entropy due to the mixture of gases of different kinds, in such a case as we have supposed, is independent of the nature of the gases.

Now we may without violence to the general laws of gases which are embodied in our equations suppose other gases to exist than such as actually do exist, and there does not appear to be any limit to the resemblance which there might be between two such kinds of gas. But the increase of entropy due to the mixing of given volumes of the gases at a given temperature and pressure would be independent of the degree of similarity or dissimilarity between them. We might also imagine the case of two gases which should be absolutely identical in all the properties (sensible and molecular) which come into play while they exist as gases either pure or mixed with each other, but which should differ in respect to the attractions between their atoms and the atoms of some other substances, and therefore in their tendency to combine with such substances. In the mixture of such gases by diffusion an increase of entropy would take place, although the process of mixture, dynamically considered, might be absolutely identical in its minutest details (even with respect to the precise path of each atom) with processes which might take place without any increase of entropy. In such respects, entropy stands strongly contrasted with energy. Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have once been mixed. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.

There is perhaps no fact in the molecular theory of gases so well established as that the number of molecules in a given volume at a given temperature and pressure is the same for every kind of gas when in a state to which the laws of ideal gases apply. Hence the quantity $\frac{pV}{t}$ in (297) must be entirely determined by the number of molecules which are mixed. And the increase of entropy is therefore determined by the number of these molecules and is independent of their dynamical condition and of the degree of difference between them.

The result is of the same nature when the volumes of the gases which are mixed are not equal, and when more than two kinds of gas are mixed. If we denote by v_1, v_2 , etc., the initial volumes of the

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different kinds of gas, and by V as before the total volume, the increase of entropy may be written in the form

$$\Sigma_1(m_1 a_1) \log V - \Sigma_1(m_1 a_1 \log v_1).$$

And if we denote by r_1, r_2 , etc., the numbers of the molecules of the several different kinds of gas, we shall have

$$r_1 = C m_1 a_1, \quad r_2 = C m_2 a_2, \quad \text{etc.},$$

where C denotes a constant. Hence

$$v_1 : V :: m_1 a_1 : \Sigma_1(m_1 a_1) :: r_1 : \Sigma_1 r_1;$$

and the increase of entropy may be written

$$\frac{\Sigma_1 r_1 \log \Sigma_1 r_1 - \Sigma_1 (r_1 \log r_1)}{C}. \quad (298)$$

The Phases of Dissipated Energy of an Ideal Gas-mixture with Components which are Chemically Related.

We will now pass to the consideration of the phases of dissipated energy (see page 140) of an ideal gas-mixture, in which the number of the proximate components exceeds that of the ultimate.

Let us first suppose that an ideal gas-mixture has for proximate components the gases G_1, G_2 , and G_3 , the units of which are denoted by $\mathfrak{G}_1, \mathfrak{G}_2, \mathfrak{G}_3$, and that in ultimate analysis

$$\mathfrak{G}_3 = \lambda_1 \mathfrak{G}_1 + \lambda_2 \mathfrak{G}_2, \quad (299)$$

λ_1 and λ_2 denoting positive constants, such that $\lambda_1 + \lambda_2 = 1$. The phases which we are to consider are those for which the energy of the gas-mixture is a minimum for constant entropy and volume and constant quantities of G_1 and G_2 , as determined in ultimate analysis. For such phases, by (86),

$$\mu_1 \delta m_1 + \mu_2 \delta m_2 + \mu_3 \delta m_3 \geq 0 \quad (300)$$

for such values of the variations as do not affect the quantities of G_1 and G_2 as determined in ultimate analysis. Values of $\delta m_1, \delta m_2, \delta m_3$ proportional to $\lambda_1, \lambda_2, -1$, and only such, are evidently consistent with this restriction: therefore

$$\lambda_1 \mu_1 + \lambda_2 \mu_2 = \mu_3. \quad (301)$$

If we substitute in this equation values of μ_1, μ_2, μ_3 taken from (276), we obtain, after arranging the terms and dividing by t ,

$$\lambda_1 a_1 \log \frac{m_1}{v} + \lambda_2 a_2 \log \frac{m_2}{v} - a_3 \log \frac{m_3}{v} = A + B \log t - \frac{C}{t}, \quad (302)$$

where

$$A = \lambda_1 H_1 + \lambda_2 H_2 - H_3 - \lambda_1 c_1 - \lambda_2 c_2 + c_3 - \lambda_1 a_1 - \lambda_2 a_2 + a_3, \quad (303)$$

$$B = \lambda_1 c_1 + \lambda_2 c_2 - c_3, \quad (304)$$

$$C = \lambda_1 E_1 + \lambda_2 E_2 - E_3. \quad (305)$$