

# PROPERTIES OF SUBSTANCES AND MIXTURES AT THE ABSOLUTE ZERO OF TEMPERATURE CONNECTED WITH CHANGE OF STATE

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## 1. Extensions of Some of the Results obtained previously

The writer in a previous paper showed<sup>1</sup> that the controllable internal energy  $u$  and the controllable entropy  $S$  are each zero for a substance or mixture in the condensed state under its vapor pressure at the absolute zero of temperature, a point called the absolute zero of control, or

$$S = 0 \quad (1)$$

$$u = 0 \quad (2)$$

under these conditions. It was also shown<sup>2</sup> that the entropy is also zero for all other states at the absolute zero of temperature. If we make use of the postulates that  $\left(\frac{\partial S}{\partial T}\right)_v$  and  $\left(\frac{\partial S}{\partial v}\right)_T$  are not discontinuous for a homogeneous mass of matter of volume  $v$  and absolute temperature  $T$ , already used in the first paper quoted, it will follow from the Calculus that

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \quad (3)$$

$$\left(\frac{\partial S}{\partial v}\right)_T = 0 \quad (4)$$

for all states of matter at the absolute zero of temperature. From these equations it can then be deduced similarly as in the papers quoted for the case that the substance is under its vapor pressure, that

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v = c_{v\infty} = 0 \quad (5)$$

$$\left(\frac{\partial^2 u}{\partial T^2}\right)_v = \left(\frac{\partial c_v}{\partial T}\right)_v = \left(\frac{\partial v_{v\infty}}{\partial T}\right)_v = 0 \quad (6)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = 0 \quad (7)$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \quad (8)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = 0 \quad (9)$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0 \quad (10)$$

$$c_p = c_{p\infty} = 0 \quad (11)$$

$$\left(\frac{\partial c_p}{\partial T}\right)_p = \left(\frac{\partial c_{p\infty}}{\partial T}\right)_p = 0 \quad (12)$$

<sup>1</sup> J. Phys. Chem., 31, 747 (1927).

<sup>2</sup> J. Phys. Chem., 31, 940 (1927).

for all states of matter at  $T = 0$ , where  $c_v$  and  $c_p$  denote the specific heat of the condensed substance at constant volume  $v$  and pressure  $p$  respectively, and  $c_{v\infty}$  and  $c_{p\infty}$  the corresponding specific heats of the vapor.<sup>1</sup>

## 2. Properties of the Heat and External Work of Evaporation at the Absolute Zero of Temperature

2. If  $L$  denote, the internal heat of evaporation of a substance or mixture and  $w$  the external work done during evaporation

$$\frac{L + w}{T} = 0 \quad (13)$$

at the absolute zero of temperature, since according to the previous Section no change in entropy takes place. Since

$$w = p(v_\infty - v_0) = RT \quad (14)$$

according to the gas equation, where  $v_\infty$  denotes the volume of the substance in the gaseous state at the absolute zero of temperature, we have

$$w = 0 \quad (15)$$

under these conditions. It follows then that

$$L = 0 \quad (16)$$

or no change in internal energy takes place during evaporation.

Another proof of this remarkable result may be based on Clapeyron's equation

$$L = \left\{ T \frac{dp}{dT} - p \right\} (v_2 - v_1) \quad (17)$$

where  $v_2$  and  $v_1$  denote the volumes of the vapor and the condensed phase respectively. This equation may be written

$$p(v_2 - v_1) = \frac{p}{T \frac{dp}{dT} - p} L \quad (18)$$

The factor of  $L$  is indeterminate in form at the absolute zero of temperature, since  $T = 0$  and  $p = 0$ . Its value can easily be found and shown to be finite by successive differentiations. Therefore since  $p(v_2 - v_1) = 0$  we have  $L = 0$ .

This result may be explained by supposing that during the separation of the molecules during evaporation attraction is the outstanding force over a certain range of distances and repulsion the outstanding force over the remaining range, and that the work done by the forces of repulsion is equal to the work done against the forces of attraction. This is rendered probable by

<sup>1</sup> Equations (9) and (10) may be obtained from equations (7) and (8) and the equations  $\left(\frac{\partial n}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$ ,  $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \frac{\partial^2 p}{\partial v \partial T} \left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial p}{\partial v}\right)_T \left\{ \frac{\partial}{\partial p} \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v - \left(\frac{\partial^2 v}{\partial T^2}\right)_p \right\}$  obtained by means of the Calculus.

considering the continuous variation of  $p$  according to an equation of state like van der Waals'. If the initial and final pressure is zero during evaporation and the process is supposed to be continuous, the pressure will at first be positive, pass through zero, become negative, and pass again through zero. The positive and negative pressures correspond to repulsion and attraction being respectively the outstanding forces between the molecules.

The result may also be explained by supposing that the molecular and atomic forces of attraction are considerably diminished if not altogether deleted on reducing the temperature to the absolute zero. Evidence that this may be the case will appear from Section 7.

Thirdly it may be explained by supposing that the work done against the atomic and molecular forces during evaporation is counterbalanced by the evolution of an equal amount of heat drawn from the intra-atomic energy. If this or the foregoing is the true explanation, the electronic configuration of the atoms in the gaseous state at the absolute zero of temperature is considerably different from that in the condensed state, and different from that in the gaseous state at higher temperatures. This is rendered highly likely by the marked changes that are predicted in Section 8 to take place in the value of the specific heat of a gas near the absolute zero of temperature. These changes are specially striking in the case of a monatomic gas since they can only be caused by changes in the electronic configurations of the atoms.

It might be argued that  $w$  or the product  $p(v_2 - v_1)$  in equation (18) may not be zero at the absolute zero of temperature. Now the factor of  $L$  in the equation is positive as can easily be shown (thus on differentiating numerator and denominator thrice with respect to  $T$  it becomes equal to  $\frac{1}{3}$ ), and hence  $L$  and  $p(v_2 - v_1)$  if finite have the same sign. But they must have different signs according to equation (13), hence we conclude that

$$w = p(v_2 - v_1) = p(v_\infty - v_0) = 0 \quad (19)$$

at the absolute zero of temperature.

Expressions for the differential coefficients of  $L$  in terms of the differential coefficients of the specific heats may be obtained on writing

$$L = u_\infty - u_0 \quad (20)$$

where  $u_\infty$  and  $u_0$  denote the internal energies in the vaporous and condensed states respectively. On differentiating this equation  $n$  times with respect to  $T$  it becomes

$$\frac{d^n L}{dT^n} = \frac{d^n u_\infty}{dT^n} - \frac{d^n u_0}{dT^n} = \frac{d^{n-1}}{dT^{n-1}} \{c_{i\infty} - c_{i0}\} \quad (21)$$

where  $c_{i\infty}$  and  $c_{i0}$  denote the internal specific heats of the vaporous and condensed states respectively. The first and second coefficient assume special values. We have

$$\frac{dL}{dT} = \frac{du_\infty}{dT} - \frac{du_0}{dT} = 0 \quad (22)$$

and

$$\frac{d^2 L}{dT^2} = \frac{d^2 u_\infty}{dT^2} - \frac{d^2 u_0}{dT^2} = 0 \quad (23)$$

according to equations (51) and (56) given in a previous paper<sup>1</sup> and extended by equations (5), (6), (7), (8), (9) and (10).

Clapeyron's equation may be written

$$\frac{L}{w} = \frac{T}{p} \frac{dp}{dT} - 1$$

The right hand side is evidently not zero but finite when  $T = 0$ , taking into account equations (36) and (37) given in the paper just quoted. On obtaining the limiting value of the left hand side by means of equations (23), (22), (16), and (15) it appears that

$$\frac{dw}{dT} = 0 \quad (24)$$

and

$$\frac{d^2w}{dT^2} = 0 \quad (25)$$

when  $T = 0$ .

Equation (13) may be written

$$\frac{L_t}{T} = 0 \quad (26)$$

where  $L_t$  denotes the total heat of evaporation, and hence we have directly

$$L_t = 0 \quad (27)$$

and

$$\frac{dL_t}{dT} = 0 \quad (28)$$

at the absolute zero of temperature, which corroborates equations (15), (16), (22) and (24).

### 3. Properties of the Condensed State at the Absolute Zero of Temperature

If a substance is passed from the state 1 to the state 2 under any given pressures at the absolute zero of temperature, we have

$$\frac{L + w}{T} = 0$$

as before, where  $L$  denotes the increase in internal energy and  $w$  the external work done. Therefore, since  $T = 0$

$$L = -w \quad (29)$$

or the increase in internal energy of a substance is equal to the external work done upon it.

If the two states are stable under their vapor pressures, which would be zero,  $w = 0$  and hence  $L = 0$  as obtained before.

<sup>1</sup> J. Phys. Chem., **31**, 937 (1927).

If we write

$$L = u_2 - u_1 \quad (30)$$

where  $u_2$  and  $u_1$  are the internal energies of the two states, one or both of which correspond to the application of an external pressure, it can be deduced that in general

$$\left( \frac{\partial^n L}{\partial T^n} \right)_p = \left[ \frac{\partial^{n-1}}{\partial T^{n-1}} \{c_{p2} - c_{p1}\} \right]_p \quad (31)$$

$$\left( \frac{\partial^n L}{\partial T^n} \right)_v = \left[ \frac{\partial^{n-1}}{\partial T^{n-1}} \{c_{v2} - c_{v1}\} \right]_v \quad (32)$$

#### 4. The Form of the Equation of State of the Vapor of a Substance at or near the Absolute Zero of Temperature

Let us write

$$w = p(v_2 - v_1) = N\beta RT \quad (33)$$

for the work of evaporation of a substance, where  $N$  denotes the total number of molecules it contains and  $\beta$  a function of  $T$  whose nature we will proceed to investigate. On differentiating the equation totally with respect to  $T$  we obtain

$$\frac{dw}{dT} = NRT \frac{d\beta}{dT} + \beta NR + \beta RT \frac{dN}{dT}$$

Hence

$$\beta = 0 \quad (34)$$

at the absolute zero of temperature according to equation (24) and since  $T = 0$ . On differentiating again we obtain

$$\frac{d^2 w}{dT^2} = NRT \frac{d^2 \beta}{dT^2} + 2NR \frac{d\beta}{dT} + 2T \frac{Rd\beta}{dT} \frac{dN}{dT} + 2\beta \frac{RdN}{dT} + \beta T \frac{Rd^2 N}{dT^2}$$

which gives

$$\frac{d\beta}{dT} = 0 \quad (35)$$

according to equations (34) and (25) and since  $T = 0$ . The differentiation may also be carried out at constant volume or constant pressure since  $\beta$  is a function of the temperature only.

$\beta$  must evidently become approximately equal to unity, for values of  $T$  not far removed from the absolute zero. This condition and equations (35) and (34) are evidently satisfied if we write

$$\beta = 1 - a^{-T^2}$$

where  $a$  is a constant greater than unity. The equation of state of the vapor of a substance close to  $T = 0$  may accordingly (provisionally) be written

$$pv = NRT(1 - a^{-T^2}) \quad (36)$$

According to the kinetic theory of gases we may write

$$pv = KNV^2 = N\beta RT$$

and hence

$$KV^2 = \beta RT \quad (37)$$

where  $V$  denotes the mean square molecular velocity and  $K$  is a constant. This equation indicates that the kinetic energy of a gas is not proportional to the temperature near the absolute zero. At the absolute zero since  $\beta = 0$  and  $T = 0$ , it is interesting to notice, the equation gives

$$V = 0 \quad (38)$$

On differentiating equation (37) twice totally with respect to  $T$  we obtain

$$2K \left\{ \left( \frac{dV}{dT} \right)^2 + V \frac{d^2V}{dT^2} \right\} = RT \frac{d^2\beta}{dT^2} + 2R \frac{d\beta}{dT}$$

At the absolute zero of temperature this equation becomes

$$\frac{dV}{dT} = 0 \quad (39)$$

according to equation (35) and since  $T = 0$  and  $V = 0$ . This equation also holds at constant volume or constant pressure. The change in molecular motion of a gas with increase in temperature at the absolute zero is thus zero, suggesting the existence of a special molecular inertness at that point.

The bearing of this result on the specific heat will appear if we consider a monatomic gas whose energy we will suppose consists of kinetic energy of motion of translation only. We will then have

$$c_{v\infty} = \frac{d}{dT} (KNV^2) = KN_2 V \frac{dV}{dT} \quad (40)$$

Thus  $c_{v\infty}$  is zero at the absolute zero of temperature if we assume, as is usually done, that the velocity of molecular motion of translation is zero, and take equation (39) into account. It is however more logical to deduce thermodynamically that  $V$  is zero (equation (38)).

On differentiating the equation with respect to  $T$  we have

$$\frac{dc_{v\infty}}{dT} = KN_2 \left( \frac{dV}{dT} \right)^2 + KN_2 V \frac{d^2V}{dT^2}$$

The right hand side is zero according to equations (38) and (39), and therefore

$$\frac{dc_{v\infty}}{dT} = 0 \quad (41)$$

Thus it appears that the properties of the specific heat of a gas expressed by equations (5) and (6) are in the case of a monatomic gas intimately connected with equations (38) and (39) referring to the velocity of molecular motion.

In the case of a complex gas we may write

$$c_{v\infty} = \frac{dT}{dT} (KNV^2) + \frac{du_{\infty}}{dT} \quad (42)$$

where  $u_{\infty}$  denotes the internal energy of the gas other than kinetic energy of motion of translation. The first term on the right hand side of the equation is zero at  $T = 0$ , as we have just seen, and hence

$$\frac{du_{\infty}}{dT} = 0 \quad (43)$$

by the help of equation (5). On differentiating the preceding equation with respect to  $T$  it can be shown on referring to equations (38), (39) and (6) that

$$\frac{d^2u_{\infty}}{dT^2} = 0 \quad (44)$$

Equations (44) and (43) also hold if the differentiations are carried out at constant volume or constant pressure since this holds for equation (39).

It is of interest to note that if we write

$$KNV^2 = RT$$

according to the old form of the gas equation, and differentiate this equation with respect to  $T$  we obtain

$$KN_2V \frac{dV}{dT} = R \quad (45)$$

Since an infinite value of  $dv/dt$  is physically absurd, at  $T = 0$  this becomes

$$0 = R$$

if we assume that  $V = 0$ . But this is inadmissible. Hence  $R$  should have a factor in the gas equation besides  $T$  which is a function of  $T$ . This factor  $\beta$  we have already shown should exist from entirely different considerations.

The gas degeneration shown by the gas equation has been suspected from the slight decrease of the specific heat at constant volume of helium as the temperature is lowered, obtained by Eucken.<sup>1</sup> It has been considered mathematically by Sackur,<sup>2</sup> Tetrode,<sup>3</sup> Keesom,<sup>4</sup> Lenz and Sommerfeld,<sup>5</sup> Scherrer,<sup>6</sup> Planck<sup>7</sup> and Nernst,<sup>8</sup> usually from the point of view of quantizing the specific heat.<sup>9</sup>

<sup>1</sup> Sitzungsber. preuss. Akad. Wiss., 144 (1912).

<sup>2</sup> Ann. Physik, (4), 40, 67 (1913).

<sup>3</sup> Physik. Z., 14, 212 (1913).

<sup>4</sup> Physik. Z., 15, 695 (1914).

<sup>5</sup> "Vorträge über die kinetische Theorie der Materie und der Elektrizität". Wolfskehl Kongress in Göttingen, p. 125, (1914).

<sup>6</sup> Göttinger Nachrichten, 8, July (1916).

<sup>7</sup> Ann. Physik., (4), 50, 385 (1916).

<sup>8</sup> "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes", p. 154, (1918).

<sup>9</sup> A purely thermodynamical treatment for temperatures not very far removed from the absolute zero has been given by the writer. J. Franklin Inst., 206, 691 (1928).

### 5. The Temperature Coefficient of the Pressure of the Saturated Vapor of a Substance or Mixture at $T = 0$ .

Let us write equation (33) in the form

$$v_2 = \frac{\beta RT}{p} \quad (46)$$

The right hand side when  $T = 0$  is indeterminate, and its limiting value is therefore

$$v_2 = \frac{\beta R + RT \frac{d\beta}{dT}}{\frac{dp}{dT}}$$

According to equations (34), (35) and equation (36) given in a previous paper<sup>1</sup>, it is still indeterminate and therefore

$$v_2 = \frac{{}_2R \frac{d\beta}{dT} + RT \frac{d^2\beta}{dT^2}}{\frac{d^2p}{dT^2}}$$

which is still indeterminate according to equation (35), equation (37) given in the paper just quoted, and since  $T = 0$ , and therefore

$$v_2 = \frac{3R \frac{d^2\beta}{dT^2} + RT \frac{d^3\beta}{dT^3}}{\frac{d^3p}{dT^3}}$$

Since  $v_2 = \infty$  when  $T = 0$  it follows from this equation that

$$\frac{d^3p}{dT^3} = 0 \quad (47)$$

This equation refers to the pressure of the saturated vapor of a condensed substance. But it should be noted that it does not follow therefore that

$$\left( \frac{d^3p}{dT^3} \right)_v = 0$$

for the condensed substance. On the other hand if this equation could be proved, equation (47) could immediately be deduced from it along the line of reasoning given in a previous paper.<sup>1</sup>

### 6. Properties of the Heat and Work of Mixing of Substances in the Gaseous State at the Absolute Zero of Temperature

Let us pass a number of condensed substances through the following isothermal cycle at the absolute zero of temperature:—

a) Mix the substances under pressures equal to their vapor pressures, giving rise to an increase in internal energy equal to  $h_m$ .

<sup>1</sup> J. Phys. Chem., 31, 937 (1927).



b) Evaporate the mixture, with attendant increase in internal energy equal to  $L$ .

c) Separate the constituents of the resultant gas from each other. The internal energy is increased by  $-h_{m\infty}$ .

d) Condense the constituents separately, giving rise to an increase in internal energy equal to  $-\Sigma L_a$ .

Since the total change in internal energy is zero

$$L - \Sigma L_a = \Delta L = h_{m\infty} - h_m \quad (48)$$

Now  $\Delta L = 0$  and  $h_m = 0$  according to equation (16) and equation (30) given in a previous paper,<sup>1</sup> and hence

$$h_{m\infty} = 0 \quad (49)$$

On differentiating equation (48) twice in succession totally with respect to  $T$  it can easily be shown by means of equations (22), (23), and equations (47) and (46) given in a previous paper<sup>1</sup> that

$$\frac{dh_{m\infty}}{dT} = 0 \text{ and } \frac{d^2h_{m\infty}}{dT^2} = 0 \quad (50)$$

We have directly that

$$\Delta \left( \frac{\partial u_\infty}{\partial T} \right)_v = \left( \frac{\partial h_{m\infty}}{\partial T} \right)_v = 0 \quad (51)$$

and

$$\Delta \left( \frac{\partial^2 u_\infty}{\partial T^2} \right)_v = \left( \frac{\partial^2 h_{m\infty}}{\partial T^2} \right)_v = 0 \quad (52)$$

by means of equations (5) and (6).

Equation (49) may be written

$$h_{m\infty} = h_f \cdot \Delta N = 0 \quad (53)$$

where  $\Delta N$  denotes the change in the number of molecules on mixing the gases, and  $h_f$  the heat absorbed corresponding to each molecule changed. Thus either  $h_f$  or  $\Delta N$  must be zero. It can easily be shown by means of equation (50) that if  $h_f$  is zero this also holds for the first and second differential coefficients with respect to  $T$ , and if  $\Delta N$  is zero this also holds for its first and second differential coefficients.

The external work  $A_\infty$  done during the process of mixing is given by

$$H_{m\infty} = h_{m\infty} + A_\infty$$

where  $H_{m\infty}$  denotes the heat absorbed during the process of mixing. Besides we have the well known equation

$$H_{m\infty} = T \left( \frac{\partial p}{\partial T} \right)_v$$

<sup>1</sup> R. D. Kleeman: J. Phys. Chem., **31**, 1559 (1927).

By means of these two equations and equations (8), (7), (49), (51), (52), and the equation  $T = 0$  it can easily be shown that

$$H_{m\infty} = 0 \text{ and } A_{\infty} = 0 \quad (54)$$

$$\left(\frac{\partial H_{m\infty}}{\partial T}\right)_v = 0 \text{ and } \left(\frac{\partial^2 H_{m\infty}}{\partial T^2}\right)_v = 0 \quad (55)$$

$$\left(\frac{\partial A_{m\infty}}{\partial T}\right)_v = 0 \text{ and } \left(\frac{\partial^2 A_{\infty}}{\partial T^2}\right)_v = 0 \quad (56)$$

## 7. Properties of the Change in Free Energy and the Heat of Formation of Substances in the Gaseous State at the Absolute Zero of Temperature

The change in free energy  $\Delta F$  is given by

$$\Delta F = \Delta u - T\Delta S + \Delta pv \quad (57)$$

If this equation is applied to gases at the absolute zero of temperature

$$\Delta u = p_{m\infty} = 0$$

and

$$\Delta pv = \Delta N\beta RT = 0$$

according to equation (49), and thus

$$\Delta F = 0 \quad (58)$$

under these conditions. On differentiating equation (57) thrice with respect to  $T$  at constant volume we have

$$\begin{aligned} \left(\frac{\partial \Delta F}{\partial T}\right)_v &= \left(\frac{\partial \Delta u}{\partial T}\right)_v - \Delta S - T\left(\frac{\partial \Delta S}{\partial T}\right)_v + \left(\frac{\partial \Delta N\beta RT}{\partial T}\right)_v, \\ \left(\frac{\partial^2 \Delta F}{\partial T^2}\right)_v &= \left(\frac{\partial^2 \Delta u}{\partial T^2}\right)_v - 2\left(\frac{\partial \Delta S}{\partial T}\right)_v - T\left(\frac{\partial^2 \Delta S}{\partial T^2}\right)_v + \left(\frac{\partial^2 \Delta N\beta RT}{\partial T^2}\right)_v, \\ \left(\frac{\partial^3 \Delta F}{\partial T^3}\right)_v &= \left(\frac{\partial^3 \Delta u}{\partial T^3}\right)_v - 3\left(\frac{\partial^2 \Delta S}{\partial T^2}\right)_v - T\left(\frac{\partial^3 \Delta S}{\partial T^3}\right)_v + \left(\frac{\partial^3 \Delta N\beta RT}{\partial T^3}\right)_v. \end{aligned}$$

From these equations we obtain

$$\left(\frac{\partial \Delta F}{\partial T}\right)_v = 0 \quad (59)$$

$$\left(\frac{\partial^2 \Delta F}{\partial T^2}\right)_v = 0 \quad (60)$$

$$\left(\frac{\partial^3 \Delta F}{\partial T^3}\right)_v = -\frac{1}{2}\left(\frac{\partial^3 u}{\partial T^3}\right)_v + 3R\left(\frac{\partial^2 \Delta \beta N}{\partial T^2}\right)_v \quad (61)$$

at the absolute zero of temperature by means of equations (1), (3), (5), (6), (35), (34) and equation (11) given in a previous paper<sup>1</sup>.

We have seen that according to equation (53) either  $\Delta N$  or  $h_f$  is zero at  $T = 0$ . If we are dealing with a finite mass of gas

$$\Delta N = 0 \quad (62)$$

according to a previous paper<sup>2</sup>.

<sup>1</sup> J. Phys. Chem., **31**, 1559 (1927).

<sup>2</sup> R. D. Kleeman: J. Franklin Inst., **206**, 691 (1928).

If however the mass of gas considered is infinite  $\Delta N$  becomes finite, if it is at all possible that  $\alpha$  molecule may exist in the gaseous state at  $T = 0$ , since  $h_m$  is zero independent of mass, the remarkable and important result is obtained from equation (53) that

$$h_f = 0 \quad (63)$$

at  $T = 0$ , or the heat of formation is zero at the absolute zero of temperature.

On differentiating equation (53) with respect to  $T$  at constant volume we obtain

$$\left(\frac{\partial \Delta N}{\partial T}\right)_v h_f + \Delta N \left(\frac{\partial h_f}{\partial T}\right)_v = \left(\frac{\partial h_{m\infty}}{\partial T}\right)_v = 0. \quad (64)$$

at  $T = 0$  according to equation (51). If as before we deal with an infinite mass of gas we obtain  $\Delta N$  finite, and since the equation holds independent of the mass of gas we obtain

$$\left(\frac{\partial h_f}{\partial T}\right)_v = 0 \quad (65)$$

by the help of equation (63). On differentiating equation (64) with respect to  $T$  at constant volume it may similarly be shown that

$$\left(\frac{\partial^2 h_f}{\partial T^2}\right)_v = 0 \quad (66)$$

by the help of equations (65), (63) and (52).

Equation (63) suggests that the atomic forces are small or disappear altogether at the absolute zero of temperature, which was also suggested by the results of Section 2. The effect of the atomic forces of attraction during combination may of course be balanced by that of repulsion, but this is hardly likely to hold in general.

## 8. Properties of the Internal Specific heat of a Vapor in Contact with the Condensed State

Let us pass a substance initially in the condensed state through the following cycle:—

a) Allow the substance to evaporate, giving rise to a change in internal energy equal to  $L$ .

b) Raise the temperature of the resultant gas by  $dT$ , giving rise to an increase in internal energy equal to  $c_{i\infty} \cdot dT$ , where  $c_{i\infty}$  denotes the internal specific heat.

c) Condense the gas, giving rise to an increase in internal energy equal to  $-(L + dL)$ .

d) Lower the temperature of the condensed substance by  $dT$ , giving rise to an increase in internal energy equal to  $c_i \cdot dT$ , where  $c_i$  denotes the internal specific heat of the condensed state.

Since the total change in internal energy is zero we have

$$c_{i\infty} = \frac{dL}{dT} + c_i \quad (67)$$

Since  $L$  is zero when  $T = 0$ ,  $\frac{dL}{dT}$  is positive up to a value  $T_m$  of the temperature given by

$$\frac{dL}{dT} = 0$$

for higher temperatures  $\frac{dL}{dT}$  is negative. Thus from the absolute zero of temperature up to the value  $T_m$  the internal specific heat of the vapor is greater than that of the condensed state, and in fact is likely to be many times greater as will be shown presently. Corresponding to the temperature  $T_m$

$$c_{i\infty} = c_i \quad (68)$$

and for higher temperatures

$$c_{i\infty} < c_i$$

If a similar cycle is carried out with the substance initially at  $T = 0$  and the temperature is then raised by  $T_m$  instead of by  $dT$ , it can easily be shown that

$$\int_0^{T_m} c_{i\infty} \cdot dT = L_m + \int_0^{T_m} c_i \cdot dT \quad (69)$$

where  $L_m$  denotes the internal heat of evaporation at the temperature  $T_m$ . On account of the large value  $L_m$  is likely to have, it follows from this equation that the average value of  $c_{i\infty}$  between 0 and  $T_m$  is likely to be many times the average value of  $c_i$ .

We saw in Section 2 that the internal heat of evaporation is zero on evaporating a substance at the absolute zero of temperature. Therefore on increasing the temperature of the vapor its potential energy of attraction is greatly increased since the internal heat of evaporation now assumes a large value. The specific heat is increased correspondingly since the increase in potential energy can only take place at the expense of heat energy absorbed from the outside. Since this also holds when the vapor is in the atomic state, an increase in temperature near the absolute zero must be attended by very pronounced changes in the electronic configuration of the atoms, which may be said to return from an abnormal state to the normal state.

## 9. The Heat of Formation of Molecules in the Gaseous State at Infinite Volume at a Finite Temperature

Let us pass a number of substances in the gaseous state at infinite volume initially at the absolute zero of temperature through the following cycle:—

a) Mix the gases. No change in internal energy takes place according to equation (63).

b) Raise the temperature of the gaseous mixture to  $T$  at constant volume. The increase in internal energy is

$$\int_0^T c_{i\infty} \cdot \partial T$$

where  $c_i$  denotes the internal specific heat.

c) Separate the gas into its constituents, which gives rise to an increase in internal energy equal to

$$- h_f \cdot \Delta N.$$

d) Lower the temperature of the gases to zero at constant volumes, giving rise to an increase in internal energy equal to

$$- \Sigma \int_0^T c_{i\infty} \cdot \partial T$$

Since the total change in internal energy is zero

$$h_f \cdot \Delta N = - \Delta \int_0^T c_{i\infty} \cdot \partial T \quad (70)$$

when we are dealing with a finite mass  $\Delta N = 0$  according to a previous paper<sup>1</sup>, but  $\Delta N$  may be finite when the mass of gas is taken infinite.

The right hand side of the foregoing equation is equal to  $-\Delta N$  multiplied by a similar integral involving a gram molecule of the complex substance in a partly dissociated state. And since we may suppose that we are dealing with a number of complex molecules equal to  $-\Delta N$  at  $T$  which remain undissociated till  $T = 0$  is reached, the foregoing equation may be written

$$h_f = - \Delta \int_0^T c'_{i\infty} \cdot \partial T \quad (71)$$

where  $\Delta c'_{i\infty}$  represents the difference between the specific heat per mol of the *undissociated* complex substance and the specific heats of its *complete* dissociation products. Hence when  $h_f$  has values above the order  $\pm 10^3$  cal. per mol the specific heat of the complex molecules has for certain temperatures abnormally large or abnormally small values depending on the sign of  $h_f$ .

#### 10. The Temperature of a Substance cannot be Reduced to the Absolute Zero in a Finite Time

Suppose that the temperature of a substance is reduced by passing it through a succession of Carnot's cycles involving a transference of heat from a low to a high temperature. Let the heat absorbed per second per unit

change of volume at the low temperature be  $\left(\frac{\partial Q}{\partial v}\right)_T$ . The heat absorbed

<sup>1</sup> J. Franklin Inst., 206, 691 (1928).

during the time  $\partial t$  is then  $T \left( \frac{\partial p}{\partial T} \right)_v \cdot \partial t$  by the help of the thermodynamical equation  $\left( \frac{\partial Q}{\partial v} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v$ . This gives rise to a drop  $\partial T$  in temperature, and accordingly

$$T \left( \frac{\partial p}{\partial T} \right)_v \cdot \partial t = -c_p \cdot \partial T$$

or

$$\partial t = \frac{c_p}{T \left( \frac{\partial p}{\partial T} \right)_v} \cdot \partial T \quad (72)$$

where  $c_p$  denotes the specific heat of the substance. Now according to equations (11), (12), (7) and (8) we may write this equation in the form

$$\partial t = - \frac{a_1 T^3}{T_1 a_2 T^3} \cdot \partial T = - \frac{a_1}{a_2} \frac{\partial T}{T}$$

close to the absolute zero of temperature, where  $a_1$  and  $a_2$  are constants. On integrating it between the limits  $t$  and  $0$ , and  $0$  and  $T$ , we obtain

$$t = \frac{a_1}{a_2} \left\{ \ln T - \ln 0 \right\} = \infty,$$

or it takes an infinitely long time to reduce the temperature of the substance from  $T$  to  $0$  in this way.

If the substance radiates like a black body it loses an amount of heat  $aT^4$  per second, and hence

$$aT^4 \cdot \partial t = -c_p \cdot \partial T$$

or

$$\partial t = - \frac{c_p}{aT^4} \cdot \partial T = \frac{a_1}{a} \frac{\partial T}{T} \quad (73)$$

where  $a$  is a constant. The integration of this equation gives

$$t = \left[ \frac{a_1}{a} \ln T \right]_0^T = \infty$$

or, as before, it takes an infinitely long time for a substance to decrease in temperature from  $T$  to  $0$  by radiation.

Thus it is hardly likely that there is matter in the Universe whose temperature is at the absolute zero unless it began that way. But since radiation of the heavenly bodies into space has been going on for millions of years, the temperature of some of them must be close to the absolute zero. Since some substances may become unstable under these conditions some interesting astronomical possibilities are opened up.

**11. The Controllable Entropy is Positive and can be Infinite only when the Temperature is Infinite.**

The entropy  $S$  of a substance at the finite temperature  $T$  and *infinite* volume is given by

$$S = \int_0^T \frac{c_{v\infty}}{T} \cdot \partial T \quad (74)$$

since the adiabetic of zero entropy corresponds to  $T = 0$ , where  $c_{v\infty}$  denotes the specific heat at constant infinite volume. The lower limit of the integral is zero according to equations (5) and (6), and hence  $S$  is *positive* and *finite*. The entropy corresponding to a *finite* volume  $v$  is given by a similar expression, which, as before is *positive* and *finite* according to equations (5) and (6). The controllable entropy is therefore a positive quantity whose value can be infinite only when the temperature is infinite.