ON THE RELATION BETWEEN PRESSURE AND EVAPORATION

BY EDWIN H. HALL

Many years ago¹ Thomson showed that the maximum vapor pressure in contact with the concave surface of a liquid, elevated by capillary action, must be less than the maximum pressure over a flat surface of the liquid at the same temperature. Maxwell's reference to this matter leaves it to be supposed that the diminution of vapor-pressure is due directly to the curvature of the surface in the tube.

But, according to views set forth by Poynting,² the maximum pressure of a vapor in contact with its liquid at a given temperature is dependent upon the total pressure to which the liquid is subjected; and Poynting attributes the smallness of the pressure above a concave surface to the small pressure borne by the liquid *just beneath* the surface. However sound Poynting's theory, his statement of it at this point lacks clearness; for the fact is apt to stick in the mind of the reader that evaporation and condensation occur, if at all, *at* the curved surface, and that this surface is subjected to the full pressure of the atmosphere; so that the pertinence of referring the state of the vapor to the state of the liquid beneath the surface is not obvious.

Le Blanc,³ although he does not mention Poynting, maintains an opinion similar to that expressed by the latter, and gives conclusive arguments in favor of it. He refers to an article by Schiller⁴ on the same subject.

¹ See Maxwell's Heat.

² Phil. Mag., July, 1881, and October, 1896.

³ Electro-Chemistry, 151, English edition.

⁴ Wied. Ann. 53, 396 (1894).

The special algebraic expression obtained below for the relation between temperature, vapor-density, and total pressure, may have been given before, although I do not remember to have seen it; but in any case I hope that the method of its derivation, by following up a commonly neglected term in a familiar operation, will possess a certain interest.

Nernst, *Theoretische Chemie*, p. 510 of the first German edition, derives the "equation of the reaction-isotherms,"

$$K = \frac{c_1^{n_1} c_2^{n_2} \dots}{c_1^{n_1} c_2^{n_2} \dots} = \text{constant},$$

in the following manner: Starting with a mixture in which the reaction occurs according to the scheme,

where every a refers to a solid or to a liquid which does not mix with the other substances present and every A to a gaseous or dissolved constituent, every ν to the number of gm. mol. of its a entering into the reaction and every n to the number of gm. mol. of its A entering into the reaction, the whole being contained in a vessel of unchanging volume, Nernst imagines the reaction to go on from left to right with no change whatever in the condition of the reaction mixture, the left-hand constituents being forced in as fast as they are consumed by the reaction and the right-hand constituents forced out as fast as they are produced. The whole operation, being carried on reversibly and isothermally, gives the same amount of work which would be given by any other reversible isothermal process proceeding from the same initial to the same final conditions. Nernst writes this amount of work thus,

$$F = -RT(n_1 \ln c_1 + n_2 \ln c_2 + \dots - n_1' \ln c_1' - n_2' \ln c_2' - \dots),$$

whence

$$F = -RT \ln \frac{c_1^{n_1} c_2^{n_2} \dots}{c_1^{n_1} c_2^{n_2} \dots} = -RT \ln K, \quad (1)$$

where each c is the concentration of the corresponding A in the

mixture. Then, as F , however the individual c 's may vary, is a constant, K must be a constant; which was the proposition to be proved.

A close examination of the conditions given by Nernst shows, however, that the value of F above given is not, in general, true. The full expression for F is ^{*}

$$F = RT/nK - RT(N - N') - P(V - V'), \quad (2)$$

where

$$\begin{aligned} N &= n_1 + n_2 + \dots, \\ N' &= n'_1 + n'_2 + \dots, \end{aligned}$$

$$\begin{aligned} V &= \text{volume of } v_1 a_1 + v_2 a_2 + \dots, \\ V' &= \text{'' '' '' } v'_1 a'_1 + v'_2 a'_2 + \dots, \end{aligned}$$

P = total pressure per unit surface within the reaction mixture.

In this amended equation, (2), the terms F and $RT(N - N')$ being constant at constant T , the only impeachment of the conclusion that RT/nK , and so K , is a constant, lies in the variation of the term $P(V - V')$ with change of P . This change, though usually small, since the whole term $P(V - V')$ is likely to be small, is unquestionable, and we must conclude that K , as defined by Nernst with reference to the c 's only, is not strictly a

*The initial condition of the A constituents outside the reaction vessel, and the final condition of the A' constituents outside the reaction vessel, is unit concentration, in gas or solution. The reversible, isothermal introduction of n_1 gm. mol. of A_1 , for example, into the reaction-vessel involves, first, isothermal expansion from density 1 to density c_1 , yielding $-n_1 RT/\ln c_1$ units of work; second, injection at constant density c_1 , through a semipermeable partition, absorbing $n_1 RT$ units of work. The net amount of work obtained from this operation is $-n_1 RT(\ln c_1 + 1)$. Similarly, the net amount of work obtained by the ejection of n'_1 gm. mol. of A'_1 at constant density c'_1 , and its subsequent compression to density 1, is $n'_1 RT(\ln c'_1 + 1)$. The equation (1), which according to Nernst shows the amount of work accomplished in the whole operation, ignores the fact that $\sum n$, or N , is not necessarily equal to $\sum n'$, or N' . We are, however, not concerned with this inaccuracy, which is, by the way, eliminated in Nernst's derivation of the equation for the "reaction-isochor." The term $P(V - V')$, which appears in (2), obviously gives the net amount of external work obtained from the injection and ejection of the solids or non-miscible liquids which take part in the operation. This amount of work is expressly put aside by Nernst as "*natürlich gleich Null*," but it is the especial point of the present discussion.

constant at constant T . Let us, therefore, take as the real equilibrium constant

$$C = K = \frac{k_1^{v_1} k_2^{v_2} \dots}{k_1^{v_1} k_2^{v_2} \dots} = K = k, \quad (3)$$

where k_1 bears the same relation to α_1 that c_1 bears to A_1 , etc.

Substituting now for K in (2), we get

$$F = RT(\ln C - \ln k) = RT(N - N') + P(V - V'), \quad (4)$$

At constant temperature the only variable terms in this equation are $RT/\ln k$ and $P(V - V')$. Hence at constant temperature

$$RT/\ln k + P(V - V') = B, \quad (5)$$

where B is a constant as regards P .

From (5) we get

$$k = e^{\frac{P(V - V') + B}{RT}}, \text{ or } \frac{k_1^{v_1} k_2^{v_2} \dots}{k_1^{v_1} k_2^{v_2} \dots} = e^{\frac{P(V - V') + B}{RT}}, \quad (6)$$

where e is the Napierian base.

Let us apply equation (6) to the case of a single liquid or solid in the presence of a gaseous phase consisting of the saturated vapor of this liquid or solid together with any number of other gases neutral to the first substance, the condensed phase of this substance being forced into an inclosure as fast, by weight, as its vapor is withdrawn, the "reaction" being simply evaporation. In this case $V' = 0$, $v_1 = 1$, and, if v_1 is the volume of 1 gm. mol. of the substance in the condensed phase, we get from (6)

$$k_1 = e^{\frac{Pv_1 + B}{RT}}, \text{ or } k_1 = e^{\frac{Pv_1}{RT}} \cdot e^{\frac{b}{RT}}, \quad (7)$$

where $b = -B$.

It will be remembered that B , and so b , is independent of P . Hence the last equation may be written

$$k_1 = e^{\frac{Pv_1}{RT}} \cdot e^{f(T)}, \quad (8)$$

$f(T)$ being some function of T .

Taking, for example, ice at -10°C as the condensed phase,

and reckoning in atmospheres and liters, we get for the vapor-density of water over the ice

$$k_1 = \epsilon \frac{P}{1100} \times \epsilon^{f(T)} \quad (9)$$

when P is very small, $\epsilon \frac{P}{1100}$ is approximately 1

"	"	1	atmos,	"	"	1.0009,
"	"	2	"	"	"	1.0018,
"	"	100	"	"	"	1.0950.

In the presence of liquid water at 0°C , we should have

$$k_1 = \epsilon \frac{P}{1240} \times \epsilon^{f(T)}, \quad \text{where } f(T) \text{ is not the same as in equation}$$

(9). In this case

when P is very small $\epsilon \frac{P}{1240}$ is approximately 1

"	"	1	atmos,	"	"	1.0008,
"	"	2	"	"	"	1.0016,
"	"	100	"	"	"	1.0840.

Of course, the same results can be found without any reference to the general "equation of the reaction-isotherm."

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