# A THEORY OF THE RATE OF SUBLIMATION.

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## Introduction.

Langmuir⑴ gave the following theoretical interpretation of the rate of sublimation. The rate of sublimation is expressed as the difference of the rate of evaporation and that of condensation, that is,

$$\text{Rate of sublimation} = \text{Rate of evaporation} - \text{Rate of condensation} \quad \ldots\ldots\ldots\ldots \quad (1),$$

and the rate of evaporation and that of condensation were expressed by the following equations respectively.

$$\text{Rate of evaporation}^{(2)} = A\sqrt{T}\,e^{-\frac{\lambda}{RT}} \quad \text{gr./cm}^2\text{./sec.} \quad \ldots\ldots\ldots \quad (2),$$

$$\text{Rate of condensation} = \alpha p\sqrt{\frac{M}{2\pi RT}} \quad \text{gr./cm}^2\text{./sec.} \quad \ldots\ldots\ldots \quad (3),$$

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(1) *J. Am. Chem. Soc.*, **38** (1916), 2221.

(2) Ibid., **35** (1913), 122; **38** (1916), 2254.

where $A$ is a constant, $T$ the absolute temperature, $\gamma$ a constant, $R$ gas constant, $\alpha$ a constant, $M$ the molecular weight, $p$ the partial pressure of the sublimed substance in the gas phase.

In the majority of cases every incident atom or molecule condenses,⁽³⁾ so that the value $\alpha$ is 1.

From equations (1), (2) and (3) we have

$$\frac{1}{S}\cdot\frac{dm}{dt}=A\sqrt{T}e^{-\frac{\lambda}{RT}}-\alpha p\sqrt{\frac{M}{2\pi RT}} \quad \ldots\ldots\ldots\ldots (4),$$

where $S$ is the area of the boundary surface, $m$ the mass of the solid sublimed. In the state of equilibrium, $dm/dt=0$. Then from equation (4) we have

$$A\sqrt{T}e^{-\frac{\lambda}{RT}}=\alpha p_\infty\sqrt{\frac{M}{2\pi RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5),$$

where $p_\infty$ is the vapour pressure of solid. From equations (4) and (5) we have

$$\frac{1}{S}\cdot\frac{dm}{dt}=\alpha\sqrt{\frac{M}{2\pi RT}}(p_\infty-p) \quad \ldots\ldots\ldots\ldots\ldots\ldots (6).$$

From equation (5) the vapour pressure of solid is given by

$$p_\infty=\frac{A}{\alpha}\sqrt{\frac{2\pi R}{M}}Te^{-\frac{\lambda}{RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7),$$

or

$$\log p_\infty=-\frac{\lambda}{2.303RT}+\log T+\log\frac{A}{\alpha}\sqrt{\frac{2\pi R}{M}} \quad \ldots\ldots\ldots\ldots (8).$$

Recently the following equation for the vapour pressure of a solid was derived by Langmuir⁽⁴⁾ by applying Dushman's theory⁽⁵⁾ for the rate of evaporation.

$$p_\infty=B\beta b\rho^{\frac{2}{3}}M^{-\frac{1}{6}}T^{\frac{1}{2}}e^{-\frac{b}{T}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9),$$

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(3) Langmuir, *J. Am. Chem. Soc.*, **54** (1932), 2801; Egerton, *Phil. Mag.*, **33** (1917), 33.

(4) *J. Am. Chem. Soc.*, **54** (1932), 2802.

(5) Ibid., **43** (1921), 397.

where $\rho$ is the density of the solid, $M$ the molecular weight, $T$ the absolute temperature, $B$, $\beta$ and $b$ constants.

## A New Theory.

Theories for the rate of solution of gas into liquid(6) and for that of solid into liquid(7) were proposed by the present writer, and the following is the application of an analogous theory to the interpretation of the mechanism of the rate of sublimation. The rate of sublimation $dn/dt$ moles/sec. is generally expressed by

$$\frac{N}{S}\frac{dn}{dt} = N_1 - N_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (10),$$

where $N$ is Avogadro's constant, $S$ the area of the boundary surface, $N_1$ the number of molecules of the substance which escape from the solid phase per unit area per unit time, $N_2$ the number of molecules which condense per unit area per unit time.

The number of molecules, whose energies of vibration at right angles to the interface lie between $\varepsilon$ and $\varepsilon + d\varepsilon$ among $N'$ molecules of the solid, is given by Maxwell's distribution law,

$$dN = \frac{N'}{kT} e^{-\frac{\varepsilon}{kT}} d\varepsilon \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (11),$$

where $k$ is Boltzmann's constant. Then the number of molecules, per unit area of the solid surface, whose energies of vibration at right angles to the interface are greater than a threshold value $\varepsilon_0$, is given by

$$N_x = \frac{N_0}{kT}\int_{\varepsilon_0}^{\infty} e^{-\frac{\varepsilon}{kT}} d\varepsilon = N_0 e^{-\frac{\varepsilon_0}{kT}} = N_0 e^{-\frac{N\varepsilon_0}{RT}} \quad \dots\dots\dots \quad (12),$$

where $N_0$ is the number of molecules which make up unit area of the solid surface.

Now an assumption is proposed. Among the molecules of which the surface of the solid is composed, only those, whose components of energy of vibration at right angles to the interface are greater than a threshold

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(6) Miyamoto, this Bulletin, **7** (1932), 8, 388; *Chem. News*, **144** (1932), 273.

(7) Miyamoto, this Bulletin, **8** (1933), 316.

value $\varepsilon_0$, are able to enter into the gas phase. Then the value $N_1$ is proportional to $N_x$ and is given by

$$N_1 = aN_0 e^{-\frac{N\varepsilon_0}{RT}} \quad \text{..................} \quad (13),$$

where $a$ is a constant. The values $\varepsilon_0$ and $N_0$ in equation (13) depend upon the specific nature of the solid and the rate of evaporation increases or decreases as the value $\varepsilon_0$ decreases or increases.

The rate of condensation is next considered, and the following assumption is proposed. Among the molecules of gas, which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value $u_0$, are able to condense on the solid surface. Then the following equation is obtained readily according to Maxwell's distribution law, as mentioned in the previous paper⁽⁷⁾.

$$N_2 = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \quad \text{...............} \quad (14).$$

From equation (3) and (14) it can be easily shown that

$$\alpha = e^{-\frac{Mu_0^2}{2RT}} \quad \text{.......................} \quad (15).$$

As above mentioned the value $\alpha$ is 1 in the majority of cases and it follows from equation (15) that the value $u_0$ is in such cases zero. From equations (10), (13) and (14) we have

$$\frac{dn}{dt} = S\left(a\frac{N_0}{N} e^{-\frac{N\varepsilon_0}{RT}} - \frac{p}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}}\right) \quad \text{.......} \quad (16).$$

Equation (16) represents the rate of sublimation according to the present theory. In the state of equilibrium, $dn/dt = 0$, and we have from equation (16).

$$\frac{aN_0}{N} e^{-\frac{N\varepsilon_0}{RT}} = \frac{p_\infty}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \quad \text{............} \quad (17),$$

where $p_\infty$ is the vapour pressure of the solid. From equations (16) and (17) we have

$$\frac{dn}{dt} = KS(p_\infty - p) \quad \text{..................} \quad (18),$$

where

$$K = \frac{1}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19).$$

Equation (18) is analogous to equation (6). It follows from equation (16) that the rate of sublimation depends upon the curvature of the solid surface, as the value $\varepsilon_0$ will be smaller when the solid surface is convex.

### The Initial Rate of Sublimation.

The initial rate of sublimation or the rate of sublimation is a vacuum is expressed by putting $p = 0$ in equation (16).

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = S\,a\frac{N_0}{N} e^{-\frac{N\varepsilon_0}{RT}} \quad \ldots\ldots\ldots\ldots\ldots \quad (20),$$

or

$$\log\left(\frac{dn}{dt}\right)_{\text{initial}} = -\frac{N\varepsilon_0}{2.303RT} + \log\frac{SaN_0}{N} \quad \ldots\ldots\ldots \quad (20)'.$$

From equations (17) and (20) we have

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{p_\infty S}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \quad \ldots\ldots\ldots\ldots\ldots \quad (21).$$

### The Vapour Pressure of Solid.

From equation (17) the vapour pressure of solid is expressed by

$$p_\infty = \frac{aN_0}{N}(2\pi MR)^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\frac{1}{RT}\left(N\varepsilon_0 - \frac{Mu_0^2}{2}\right)} \quad \ldots\ldots\ldots \quad (22),$$

or

$$\log p_\infty = -\frac{Q}{2.303RT} + \frac{1}{2}\log T + C \quad \ldots\ldots\ldots\ldots\ldots \quad (22)',$$

where

$$Q = N\varepsilon_0 - \frac{Mu_0^2}{2},$$

$$C = \log \frac{aN_0\sqrt{2\pi MR}}{N}.$$

From equation (22) it follows that the vapour pressure of a convex surface is greater than that of plane surface, as the value $\varepsilon_0$ will be smaller in the former case according to the present theory.

Now the value $N_0$, the number of molecules which make up unit area of the solid surface, is normally given by

$$N_0 = \gamma\left(\frac{N}{v_m}\right)^{\frac{2}{3}} = \gamma\left(\frac{\rho N}{M}\right)^{\frac{2}{3}} \quad \ldots\ldots\ldots\ldots\ldots \quad (23),$$

where $N$ in Avogadro's constant, $v_m$ the molar volume, $\rho$ the density of the solid, $M$ the molecular weight, $\gamma$ a constant, the value of which depends upon the arrangement of the molecules of solid. From equations (22) and (23) we have

$$p_\infty = a\gamma N^{-\frac{1}{3}}(2\pi R)^{\frac{1}{2}}\rho^{\frac{2}{3}}M^{-\frac{1}{6}}T^{\frac{1}{2}}e^{-\frac{1}{RT}\left(N\varepsilon_0-\frac{Mu_0^2}{2}\right)} \quad \ldots\ldots \quad (24).$$

Thus an equation analogous to equation (9) is obtained according to the present theory.

The writer's intension is to apply this new theory to the interpretation of the mechanism of adsorption on a subsequent occasion.

## Summary.

A theory of the rate of sublimation was proposed, which is based upon the assumptions, that among the molecules, which make up the solid surface, only those, whose energies of vibration at right angles to the interface are greater than a threshold value $\varepsilon_0$ can escape from the solid phase, and that among the molecules in the gas phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value $u_0$, can condense on the solid surface.

On the basis of this theory the following equations have been derived for the rate of sublimation and for the vapour pressure of solid.

$$\frac{dn}{dt} = S\left(\frac{aN_0}{N}e^{-\frac{N\varepsilon_0}{RT}} - \frac{p}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}\right),$$

$$p_\infty = a\frac{N_0}{N}(2\pi MR)^{\frac{1}{2}}T^{\frac{1}{2}}e^{-\frac{1}{RT}\left(N\varepsilon_0-\frac{Mu_0^2}{2}\right)},$$

or

$$p_\infty = a\gamma N^{-\frac{1}{3}}(2\pi R)^{\frac{1}{2}}\rho^{\frac{2}{3}}M^{-\frac{1}{6}}T^{\frac{1}{2}}e^{-\frac{1}{RT}\left(N\varepsilon_0-\frac{Mu_0^2}{2}\right)}.$$

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