



A method of statistical mechanical treatment of equilibrium and chemical reactions^{☆,☆☆}

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1. Introduction

The present paper is concerned with a method of treating equilibrium and chemical reaction by introducing a set of conjugated statistical mechanical functions defined, respectively, as the factor of multiplication of the Zustandsumme caused by increasing a certain constituent of the assembly of interest or by imposing a microscopic constraint upon the elementary state of the constituent.

Okamoto et al. [1] have previously introduced the functions p^δ and q_σ^δ of this sort in their statistical mechanical treatment of the hydrogen electrode process. Among these p^δ is related, as shown later, to the chemical potential μ^δ , as

$$\mu^\delta = -RT \log p^\delta$$

which was originally introduced by Gibbs [2] in terms of classical grand canonical ensemble, whereas p^δ is defined here, according to Gibbs' terminology, in

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terms of petit canonical ensemble. The function is introduced in the latter way independently by Kirkwood [3,4] and applied to the statistical mechanics of the condensed fluid in equilibrium. The function q_σ^δ has, on the other hand, no corresponding thermodynamical quantity.

In the present paper, we are going to introduce, in extension of the theory of p^δ and q_σ^δ , a complete set of four conjugated functions and give several examples of application of the equilibrium and chemical reaction.

2. Definitions and approximations

2.1. The assembly and parameters

Our object of treatment will be a macroscopic assembly composed of molecules of several kinds, whose set of quantum mechanical Eigenwerts being fixed by several independent parameters. The parameters may be the volume confining the total extension of the assembly, the electrostatical or magnetic field within which the whole assembly is situated. These parameters which are quantities accessible to the direct macroscopic measurements will specially be termed external ones in distinction from internal parameters later referred to which, being inaccessible

to direct macroscopic measurements, restrict microscopic states of individual molecules. The macroscopic assembly will be denoted by C in general.

The assembly will be termed in statistical equilibrium when its properties are derivable from the appropriate petit quantum canonical ensemble. The Zustandsomme (abbreviated Zs hereafter) appropriate to any equilibrium state of C is expressed by

$$QC = \sum_n e^{-E_n/kT}, \quad (2.1)$$

where k is Boltzmann's constant and E_n the n th Eigenwert.

The molecule in the above sense may consist in any elementary particles or any group of elementary particles bound closely together, however, not being necessarily dynamically isolated from the environment. By molecule will thus be meant hereafter not only gaseous molecule in its original sense, but also such an elementary particle or a group of elementary particles in a liquid phase under the strong influence of surrounding ones or even such one bound chemically on the surface of a solid.

2.2. Four conjugated functions, p^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$, and $\Theta_{\sigma(0)}$

We define p^δ by

$$p^\delta = \frac{QC_0^\delta}{QC_0}, \quad (2.2)$$

where QC_0 is Zs of our assembly C_0 free, in particular, from any microscopic constraints, and QC_0^δ that of C_0^δ , which is C_0 augmented by a molecule or a set of molecules δ with fixed external parameters. The function q_σ^δ is defined by

$$q_\sigma^\delta = \frac{QC_{\sigma(\delta)}^\delta}{QC_{\sigma(0)}}, \quad (2.3)$$

where $QC_{\sigma(\delta)}^\delta$ or $QC_{\sigma(0)}$ is Zs of the assembly $C_{\sigma(\delta)}^\delta$ or $C_{\sigma(0)}$, respectively, subject to the microscopic constraint, i.e. a particular elementary state σ for a single piece of molecule δ or a set σ of states each for individual piece of a set δ of molecules is occupied by δ or vacant. The elementary state σ or the individual state of the set σ may be a small cavity of molecular dimension confining the centre of gravity of a molecule

or a certain quantum state for the energy or the momentum of the latter.

We define further two quantities in terms of the Zs's appeared in Eqs. (2.2) and (2.3) as

$$\Theta_{\sigma(\delta)} = \frac{QC_{\sigma(\delta)}^\delta}{QC_0^\delta} \quad (2.4)$$

and

$$\Theta_{\sigma(0)} = \frac{QC_{\sigma(0)}}{QC_0}. \quad (2.5)$$

$\Theta_{\sigma(\delta)}$ or $\Theta_{\sigma(0)}$ has thus the physical meaning of the respective probability that σ is occupied or evacuated by δ .

2.3. Extension of the definitions

The above defined functions may also be termed the respective factors of multiplication of Zs caused by the appropriate operations; p^δ is thus the factor due to the operation of adding δ to the assembly C_0 with unconstrained internal parameters bringing about thereby an assembly C_0^δ of the same description but with one more constituent molecule δ , q_σ^δ that of bringing one additional δ up into vacant σ of $C_{\sigma(0)}$ and $\Theta_{\sigma(\delta)}$ or $\Theta_{\sigma(0)}$ that of imposing the constraint upon the unconstrained assembly C_0^δ or C_0 that a specified state σ is, respectively, occupied by δ or evacuated with certainty.

With this interpretation above definitions may be expressed in the forms

$$\log p^\delta = \Delta_{p,\delta} \log QC_0, \quad (2.6)$$

$$\log q_\sigma^\delta = \Delta_{q,\sigma(0)} \log QC_{\sigma(0)}, \quad (2.7)$$

$$\log \Theta_{\sigma(\delta)} = \Delta_{\Theta,\sigma(0)} \log QC_0^\delta, \quad (2.8)$$

$$\log \Theta_{\sigma(0)} = \Delta_{\Theta,\sigma(0)} \log QC_0, \quad (2.9)$$

or summarized as

$$\log \lambda = \Delta_\lambda \log QC, \quad (2.10)$$

where λ stands for p^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$ or $\Theta_{\sigma(0)}$ and Δ_λ , when prefixed for instance to $\log QC$, gives the increment caused by the operation appropriate to λ . For the sake of having any meaning for the quantity with the prefix, the assembly of interest must however be accessible to the operation associated with λ . It is meant by

“accessible”, for instance, to the operation associated with q_σ^δ that the assembly $C_{\sigma(0)}$, $C_{\sigma(0)}^\delta$ or such other has σ free to accept δ or the operation associated with $\Theta_{\sigma(\delta)}$ that C_0 , C^δ 's are, not being constrained by any prescribed condition, ready to access the operation of filling up σ with δ with certainty.

We define $\Delta_\lambda P$ as the increment of any property P accompanied by the operation Δ_λ upon the assembly, and the quantity prefixed with $\Delta_{p,\lambda}$ for instance $\Delta_{p,\lambda} \log QC$ as that of $\log QC$ caused by increasing P alone by the amount $\Delta_\lambda P$ without virtual operation.

These increment defined above will be called first-order increments. Denoting any two of these Δ 's by Δ_1 and Δ_2 we define second-order increment $\Delta_1 \Delta_2 \log QC \equiv \Delta_1 \log QC(\Delta_2) - \Delta_1 \log QC$ and $\Delta_1 \Delta_2 P \equiv \Delta_1 P(\Delta_2) - \Delta_1 P$, where $C(\Delta_2)$ is the assembly brought about from C by the operation associated with Δ_2 and $P(\Delta_2)$ the appropriate value of P , it being presupposed that both C and $C(\Delta_2)$ are accessible to the operation Δ_1 . Similarly, we define higher order increments.

2.4. Approximations

Throughout the present paper, we will be contented with the approximation of neglecting increments of higher than second-order or power compared with the increment of first-order or power except when the direct interaction between two molecules each at an elementary state σ_1 or σ_2 , respectively, specified, if at all, by the two operations involved, such as in the case when $\Delta_1 \equiv \Delta_{\Theta, \sigma_1(\delta)}$ and $\Delta_2 \equiv \Delta_{\Theta, \sigma_2(\delta)}$, is significant. If either or both of the operation are of the sort $\Delta_{p,\delta}$, which specifies no elementary state, this exception falls of course off.

It follows that

$$(i) \Delta_{p,\delta_2}(\log QC_0 + \Delta_{p,\delta_1} \log QC_0) = \Delta_{p,\delta_2} \log QC_0.$$

But since according to Eqs. (2.2) and (2.6), it is

$$\log QC_0 + \Delta_{p,\delta_1} \log QC_0 = \log QC_0^{\delta_1},$$

we have,

$$\frac{QC_0^{\delta_1 + \delta_2}}{QC_0^{\delta_1}} = \frac{QC_0^{\delta_2}}{QC_0}.$$

Writing $p^{\delta_1 + \delta_2}$ for the set of molecules $\delta_1 + \delta_2$ according to Eq. (2.2) in the form,

$$p^{\delta_1 + \delta_2} = \frac{QC_0^{\delta_1 + \delta_2}}{QC_0} = \frac{QC_0^{\delta_1 + \delta_2}}{QC_0^{\delta_1}} \frac{QC_0^{\delta_1}}{QC_0}$$

we have

$$p^{\delta_1 + \delta_2} = p^{\delta_1} p^{\delta_2}.$$

It may similarly be shown for a set δ of several molecules,

$$\delta = \sum_g v_g \delta_g$$

consisting each v_g pieces of δ_g ,

$$p^\delta = \prod_g (p^{\delta_g})^{v_g}. \quad (2.11)$$

(ii) We have similarly as in the case of (i),

$$\begin{aligned} \Delta_{\Theta, \sigma(\delta)}(\log QC_0 + \Delta_{p,\delta} \log QC_0) \\ = \Delta_{\Theta, \sigma(\delta)} \log QC_0, \end{aligned}$$

or according to Eqs. (2.4) and (2.8),

$$\Theta_{\sigma(\delta)} = \frac{QC_{\sigma(\delta)}^\delta}{QC_0^\delta} = \frac{QC_{\sigma(\delta)}}{QC_0}. \quad (2.12)$$

(iii) Any increment of $\log QC$ may be written in the form,

$$\Delta_\lambda \log QC = (\Delta_\lambda \log QC)_P + \sum_j \Delta_{P_j, \lambda} \log QC,$$

where the $(\Delta_\lambda \log QC)_P$ denotes the increment in the case when all properties P_j 's of interest are arrested. Expanding $\Delta_{P_j, \lambda} \log QC$ in power series of $\Delta_\lambda P_j$ and rejecting terms higher than the first power, we have,

$$\Delta_{P_j, \lambda} \log QC = \frac{\partial \log QC}{\partial P_j} \Delta_\lambda P_j$$

and hence

$$\begin{aligned} \Delta_\lambda \log QC = (\Delta_\lambda \log QC)_P \\ + \sum_j \frac{\partial \log QC}{\partial P_j} \Delta_\lambda P_j. \end{aligned} \quad (2.13)$$

3. Theory

3.1. Interrelation among p^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$ and $\Theta_{\sigma(0)}$

It follows immediately from Eqs. (2.2)–(2.5)

$$q_\sigma^\delta = \frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(0)}} p^\delta. \quad (3.1)$$

If δ consists in a single molecule and σ a small cavity of molecular dimension which restricts the centre of gravity of δ within, the above equation may be written in the form,

$$p^\delta = \Theta_{\sigma(0)} \frac{q_\sigma^\delta / |\sigma|}{\Theta_{\sigma(\delta)} / |\sigma|}, \quad (3.2)$$

where $|\sigma|$ is the size of the cavity σ . As $|\sigma|$ approaches zero, so does $\Theta_{\sigma(0)}$ unity and $\Theta_{\sigma(\delta)} / |\sigma|$ the limiting ratio of the probability finding the centre of gravity of the molecule of the kind δ in the cavity to its volume or the concentration N^δ at the point of convergence, i.e.

$$N^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\Theta_{\sigma(\delta)}}{|\sigma|}. \quad (3.3)$$

Since p^δ should remain the same by definition irrespective of the arbitrarily assigned magnitude $|\sigma|$, $q_\sigma^\delta / |\sigma|$ tends to a definite value along with $\Theta_{\sigma(\delta)} / |\sigma|$. Denoting the limiting value by Q^δ , i.e. putting

$$\lim_{|\sigma| \rightarrow 0} \frac{q_\sigma^\delta}{|\sigma|} = Q^\delta. \quad (3.4)$$

We have Eq. (2.2) in the form,

$$p^\delta = \frac{Q^\delta}{N^\delta}. \quad (3.5)$$

3.2. Equilibrium relation for p^δ

Let the condition prescribed to the assembly be such that δ may exist in different states, δ^A , δ^B , etc., QC^{δ^A} , QC^{δ^B} , etc. are now of the same value, since it is the immaterial for the Zs over all possible states of the assembly, whatever state δ may initially assume when admitted. It follows by Eq. (2.2)

$$p^{\delta^A} = p^{\delta^B} = \text{etc.} \quad (3.6)$$

The states δ^A , δ^B , etc. will be called in equilibrium with each other.

If δ^A , δ^B , etc. are, respectively, such sets of molecules as

$$\delta^A = \sum_a v_a^A \delta_a^A, \quad \delta^B = \sum_b v_b^B \delta_b^B,$$

i.e. consist, respectively, of v_a^A , v_b^B , etc. pieces of individual molecules δ_a^A , δ_b^B , etc., we have by Eqs. (2.11) and (3.6)

$$\prod_a (p^{\delta_a^A})^{v_a^A} = \prod_b (p^{\delta_b^B})^{v_b^B}. \quad (3.7)$$

3.3. Force, work, and energy

We postulate that there exists a set of internal parameters such that by varying the latter continuously independent of each other and of the external ones, the microscopic state of constituent molecules is transferred from one to the other keeping the whole assembly at every instant at the statistical equilibrium. The assembly C_0 may thus be converted into $C_{\sigma(\delta)}$ or $C_{\sigma(0)}$ and the assembly consisting of macroscopic assembly C_0 or $C_{\sigma(0)}$ and a molecule δ each situated outside the influence of the other, i.e. $C_0 + \delta$ or $C_{\sigma(0)} + \delta$ may thus be unified into C_0^δ or $C_{\sigma(0)}^\delta$. All parameters including internal and external ones will be denoted by α_a 's. We have then according to Eq. (2.1)

$$-kT \log \frac{QC_{II}}{QC_{I}} = \sum_a \int_{\alpha_a(I)}^{\alpha_a(II)} (-\Pi_{\alpha_a}) d\alpha_a, \quad (3.8)$$

where

$$\Pi_{\alpha_a} = \frac{\partial(kT \log QC)}{\partial \alpha_a} = \frac{\sum_n -(\partial E_n / \partial \alpha_a) e^{-E_n/kT}}{\sum_n e^{-E_n/kT}}. \quad (3.9)$$

Suffixes I and II signify two different particular states of our assembly, and $\alpha(I)$ and $\alpha(II)$ appropriate values of the parameters α_a . The partial differential coefficient $-\partial E_n / \partial \alpha_a$ is the force with which the assembly at n th quantum state tends to increase with the parameter α_a , Π_{α_a} the statistical average of the force, $-\Pi_{\alpha_a}$ the force to be applied from the external world to the assembly to keep α_a constant, and, in consequence the left-hand side of Eq. (3.8) the work required to bring up the assembly from the state I to II

keeping the latter throughout at statistical equilibrium. The Π_{α_a} will be called the average force conjugated to the parameter α_a and the work the reversible work.

In the particular case when

$$C_I = C_0 + \delta \quad \text{and} \quad C_{II} = C_0^\delta$$

the left-hand side of Eq. (3.8) is $-kT \log p^\delta$,¹ which equals the relevant reversible work on the right. The function $-kT \log q_\sigma^\delta$ is similarly the reversible work required with fixed external parameters of $C_{\sigma(0)}$ to bring up δ from the standard state into the preliminarily evacuated state σ , and $-kT \log \Theta_{\sigma(0)}$ or $-kT \log \Theta_{\sigma(\delta)}$ that required to force upon the assembly C_0 the constraint that σ is, respectively, vacant or occupied by δ with certainty. The latter three reversible works naturally correspond to no readymade thermodynamical quantity because of its microscopically detailed nature.

These reversible works $-kT \log p^\delta$, $-kT \log q_\sigma^\delta$, $-kT \log \Theta_{\sigma(\delta)}$ and $-kT \log \Theta_{\sigma(0)}$ are summarized, according to Eq. (2.10), by

$$-kT \log \lambda = \Delta_\lambda(-kT \log QC), \quad (3.10)$$

or by

$$-RT \log \lambda = \Delta|_\lambda(-kT \log QC), \quad (3.11)$$

where $\Delta|_\lambda$ signifies Avogadro's number N_A times the increment Δ_λ .

The temperature variation of QC at fixed external parameter α_a 's is as well-known expressed according to Eq. (2.1) in terms of statistical average \bar{E} of Eigenwerts, i.e.

$$kT^2 \frac{\partial \log QC}{\partial T} = \frac{\sum_n E_n e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} = \bar{E}. \quad (3.12)$$

Partial differential coefficients with respect to T without suffix will hereafter be referred to fixed external parameters. The temperature variation of λ is henceforth expressed according to Eqs. (3.11) and (3.12), as

$$RT^2 \frac{\partial \log \lambda}{\partial T} = \Delta|_\lambda \bar{E}. \quad (3.13)$$

¹ Since $Q(C_0 + \delta)$ may be factored as $Q(C_0 + \delta) = Q(C_0)Q\delta$, we have $QC_{II}/QC_I = QC_0^\delta/QC_0$ by choosing as $Q\delta = 1$.

3.4. The functions and associated relations in thermodynamical terminology

Provided that the statistical equilibrium fully describes the thermodynamical equilibrium, $-kT \log QC$ may be identified with Helmholtz free energy F according to Eq. (3.8) and \bar{E} with the internal energy U in thermodynamics, so that

$$F = -kT \log QC \quad (3.14)$$

and

$$U = kT^2 \frac{\partial \log QC}{\partial T}. \quad (3.15)$$

We have immediately according to Eqs. (3.14) and (3.15)

$$U = F - T \frac{\partial F}{\partial T}, \quad (3.16)$$

from Eq. (3.9)

$$-\Pi_{\alpha_a} = \frac{\partial F}{\partial \alpha_a}, \quad (3.17)$$

from Eq. (3.11)

$$\Delta|_\lambda F = -RT \log \lambda, \quad (3.18)$$

and from Eq. (3.13)

$$\Delta|_\lambda U = RT^2 \frac{\partial \log \lambda}{\partial T}, \quad (3.19)$$

or from Eq. (3.16)

$$\Delta|_\lambda U = \Delta|_\lambda F - T \frac{\partial \Delta|_\lambda F}{\partial T}. \quad (3.20)$$

Defining the entropy to complete the thermodynamical terminology as²

$$S = -\frac{\partial F}{\partial T}, \quad (3.21)$$

² The present argument is evidently valid in particular in the case of microcanonical ensemble, when all quantum states have the same Eigenwert E_n . In that case, Eq. (3.14) reduces, according to Eq. (2.1) to the form,

$$F = E_n - kT \log \sum_n 1,$$

whence we have by Eq. (3.21), $S = k \log \sum_n 1$. This is the quantum mechanical transcription of the well-known Boltzmann's relation.

we have readily

$$\Delta|_{\lambda}S = -\frac{\partial \Delta|_{\lambda}F}{\partial T} \quad (3.22)$$

and from Eq. (3.16)

$$F = U - TS \quad (3.23)$$

or

$$\Delta|_{\lambda}F = \Delta|_{\lambda}U - T\Delta|_{\lambda}S. \quad (3.24)$$

In the special case when $\lambda = p^{\delta}$, the reversible work $-RT \log p^{\delta}$ may be identified with the chemical potential μ^{δ} in thermodynamics so that

$$\mu^{\delta} = -RT \log p^{\delta}. \quad (3.25)$$

Eqs. (3.18)–(3.20), (3.22) and (3.24) then assume, respectively, the forms, i.e.

$$(3.18) \quad \mu^{\delta} = \bar{F}^{\delta}, \quad (3.26)$$

$$(3.19) \quad RT^2 \frac{\partial \log p^{\delta}}{\partial T} = \bar{U}^{\delta}, \quad (3.27)$$

$$(3.20) \quad \bar{U}^{\delta} = \mu^{\delta} - T \frac{\partial \mu^{\delta}}{\partial T}, \quad (3.28)$$

$$(3.22) \quad \bar{S}^{\delta} = -\frac{\partial \mu^{\delta}}{\partial T}, \quad (3.29)$$

$$(3.24) \quad \mu^{\delta} = \bar{U}^{\delta} - T\bar{S}^{\delta}, \quad (3.30)$$

where \bar{F}^{δ} , \bar{U}^{δ} and \bar{S}^{δ} denote, respectively, $\Delta|_{p,\delta}F$, $\Delta|_{p,\delta}U$ and $\Delta|_{p,\delta}S$ ³ and called in accordance with G.N. Lewis partial molar free energy, partial molar internal energy and partial molar entropy, respectively.

Our approximation (i), Section 2.4, assumes now the form,

$$\mu^{\delta} = \sum_g v_g \mu^{\delta_g}$$

which is taken as a matter of course in thermodynamics.

3.5. The λ for the assembly with variable external parameters

In the foregoing section λ 's have been defined with regard to an assembly whose external parameters are kept constant throughout the operation associated with respective λ 's. We extend here their definition and

³ cf. Eq. (2.6).

theory to the case when the external parameters of the assembly of interest are not necessarily kept constant.

Let an assembly of interest A , which exclusively subject to the operation associated with λ , is coupled with another K according to the condition that (i) each external parameter which is extensive property such as volume, surface area, etc. is not fixed individually with A and K but by the sum of that, β_b , of A and that of K , whereas external parameters of other kind is fixed individually (ii) no force conjugated with β_b 's acts upon $A + K$ from outside and that (iii) energy states of either assembly is individually fixed dynamically independent of each other at fixed values of β_b 's. A simple example of such an assembly is that consisting of two gaseous parts A and K sealed in a cylinder and separated by a frictionless piston left free to move; the energy state of the either gas may be taken as determined by the volume of A , which is the only external parameter of the latter proper, and no force conjugated to the parameter is exerted by the external world.

We have thus in the assembly $A + K$ the special case of that dealt with in the foregoing sections, for which, of course, all definitions and consequent theoretical developments remain valid. The same is true with the assembly A alone provided that β_b 's are arrested. The latter assembly will be denoted A_{β} .

We may thus define λ 's either with the assembly $A + K$ or with A_{β} specifying the assembly C of Eq. (2.10) to be either $A + K$ or A_{β} . Former ones will be called λ 's of assembly of variable external parameters or simply those of $A + K$ and latter those of A_{β} .

In the following section, we will first show the identity of the two series of λ 's of the alternative definitions (Section 3.6) next transform λ 's of $A + K$ with special reference to the interested assembly A (Section 3.7) and finally put the resulting expressions in comparison with those for λ 's of A_{β} into thermodynamical terminology (Section 3.8).

3.6. Identity of λ 's of the assembly $A + K$ and those of A_{β}

The $\log \lambda$ is expressed λ according to Eq. (2.13) in the form,

$$\log \lambda = \Delta_{\lambda} \log Q(A + K) = (\Delta_{\lambda} \log Q(A + K))_{\beta} + \sum_b \frac{\partial \log Q(A + K)}{\partial \beta_b} \Delta_{\lambda} \beta_b, \quad (3.31)$$

where suffix β signifies the condition of fixed β_b 's and $\Delta_\lambda \beta_b$ the increments of β_b 's under the specified condition of $A + K$. The differential coefficient $\partial \log Q(A + K) / \partial \beta_b$ is however according to Eq. (3.9) the force conjugated to β_b multiplied by $1/kT$, which vanishes according to (ii), Section 3.5, i.e.

$$\frac{\partial \log Q(A + K)}{\partial \beta_b} = 0 \quad (3.32)$$

and hence the second term on the third member of Eq. (3.31) vanishes.

The first term $(\Delta_\lambda \log Q(A + K))_\beta$ is expressed in the form,

$$(\Delta_\lambda \log Q(A + K))_\beta = \Delta_\lambda \log Q A_\beta + (\Delta_\lambda \log Q K)_\beta, \quad (3.33)$$

where

$$(\Delta_\lambda \log Q K)_\beta = 0, \quad (3.34)$$

since A is only subjected to the operation.

We have by Eqs. (3.31)–(3.34)

$$\log \lambda = \Delta_\lambda \log Q(A + K) = \Delta_\lambda \log Q A_\beta \quad (3.35)$$

which states the enunciated identity.

3.7. Expression of λ and derived quantities with special reference to A

We begin with the expression for $-kT \log Q(A + K)$ with special reference to the assembly A . According to (iii), Section 3.5, $Q(A + K)$ is factored in the form,

$$Q(A + K) = Q A Q K \quad (3.36)$$

and $Q K$ in turn expressed according to Eq. (3.8) as

$$\log Q K = \frac{1}{kT} \sum_b \int_{\beta_b(0)}^{\beta_b} \Pi_{\beta_b}^K d\beta_b + \log Q K_{\beta(0)}, \quad (3.37)$$

where $\Pi_{\beta_b}^K$ is the average force of the assembly K conjugated to β_b and $K_{\beta(0)}$ the assembly K fixed by a particular set of values $\beta_b(0)$'s of β_b 's.

We have, on the other hand, according to Eqs. (3.9), (3.32) and (3.36),

$$\Pi_{\beta_b}^A + \Pi_{\beta_b}^K = 0, \quad (3.38)$$

where $\Pi_{\beta_b}^A$ is the force of the assembly A conjugated with β_b . Substituting $\Pi_{\beta_b}^K$ from Eq. (3.38) into

Eq. (3.37), we have

$$\log Q K = -\frac{1}{kT} \sum_b \int_{\beta_b(0)}^{\beta_b} \Pi_{\beta_b}^A d\beta_b + \log Q K_{\beta(0)} \quad (3.39)$$

and substituting the latter in turn into Eq. (3.36)

$$\begin{aligned} \log Q(A + K) &= \log Q A - \frac{1}{kT} \sum_b \int_{\beta_b(0)}^{\beta_b} \Pi_{\beta_b}^A d\beta_b \\ &\quad + \log Q K_{\beta(0)}. \end{aligned} \quad (3.40)$$

Eq. (3.40) expresses $\log Q(A + K)$ in term of variables appropriate to A , $\log Q K_{\beta(0)}$ being thereby a constant.

Eqs. (2.10) and (3.40) give now according to Eq. (2.13),

$$\begin{aligned} \log \lambda &= \Delta_\lambda \log Q A - \frac{1}{kT} \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \Pi_{\beta_b}^A d\beta_b \\ &\quad - \frac{1}{kT} \sum_b \Pi_{\beta_b}^A \Delta_\lambda \beta_b, \end{aligned} \quad (3.41)$$

where $\Delta_\lambda \Pi_{\beta_b}^A$ is the increment of the force $\Pi_{\beta_b}^A$ due to the operation associated with λ .

The temperature variation of $Q(A + K)$ and of λ is now derived beginning again with that of $Q(A + K)$. We have according to Eqs. (3.32) and (3.36)

$$\begin{aligned} \frac{\partial \log Q(A + K)}{\partial T} &= \left(\frac{\partial \log Q(A + K)}{\partial T} \right)_\beta + \sum_b \frac{\partial \log Q(A + K)}{\partial \beta_b} \frac{\partial \beta_b}{\partial T} \\ &= \left(\frac{\partial \log Q A}{\partial T} \right)_\beta + \left(\frac{\partial \log Q K}{\partial T} \right)_\beta, \end{aligned} \quad (3.42)$$

or expressing $(\partial \log Q K / \partial T)_\beta$ by Eq. (3.39)

$$\begin{aligned} kT^2 \left(\frac{\partial \log Q(A + K)}{\partial T} \right)_\beta &= kT^2 \left(\frac{\partial \log Q A}{\partial T} \right)_\beta + \sum_b \int_{\beta_b(0)}^{\beta_b} \Pi_{\beta_b}^A d\beta_b \\ &\quad - T \sum_b \int_{\beta_b(0)}^{\beta_b} \frac{\partial \Pi_{\beta_b}^A}{\partial T} d\beta_b + kT^2 \left(\frac{\partial \log Q K_{\beta(0)}}{\partial T} \right)_\beta, \end{aligned} \quad (3.43)$$

where the partial differential coefficient without suffix denotes those under the specified condition of $A + K$ in distinction from those with suffix β at fixed β_b 's.

The temperature variation of λ is expressed according to Section 2.4, Eqs. (2.10) and (3.43) as

$$\begin{aligned} kT^2 \frac{\partial \log \lambda}{\partial T} &= kT^2 \Delta_\lambda \left(\frac{\partial \log \mathcal{Q}A}{\partial T} \right)_\beta + \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \Pi_{\beta_b}^A d\beta_b \\ &+ \sum_b \Pi_{\beta_b}^A \Delta_\lambda \beta_b - T \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \frac{\partial \Pi_{\beta_b}^A}{\partial T} d\beta_b \\ &- T \sum_b \frac{\partial \Pi_{\beta_b}^A}{\partial T} \Delta_\lambda \beta_b. \end{aligned} \quad (3.44)$$

Eq. (3.44) is of course directly obtained by the differentiation of Eq. (3.41). The temperature variation of λ defined with respect to assembly A^4 is expressed according to Eqs. (2.10), (3.34) and (3.36) as

$$kT^2 \left(\frac{\partial \log \lambda}{\partial T} \right)_\beta = kT^2 \Delta_\lambda \left(\frac{\partial \log \mathcal{Q}A}{\partial T} \right)_\beta. \quad (3.45)$$

Comparing Eq. (3.44) with Eq. (3.45), we see that whereas λ 's of the two alternative definition are identical as shown in Section 3.6, their temperature variation are different in general.

3.8. Thermodynamical form of λ 's and associated quantities for the assembly of variable external parameters

We first write down Helmholtz free energy and the internal energy, respectively, according to Eq. (3.14) and to Eq. (3.15) of the assemblies, $A + K$, A and $K_{\beta(0)}$ with appropriate subscripts, i.e.⁵

$$F = -kT \log \mathcal{Q}(A + K), \quad (3.46.AK)$$

$$F_A = -kT \log \mathcal{Q}A, \quad (3.46.A)$$

$$F_{K,\beta(0)} = -\log \mathcal{Q}K_{\beta(0)}, \quad (3.46.K)$$

$$U = kT^2 \frac{\partial \log \mathcal{Q}(A + K)}{\partial T}, \quad (3.47.AK)$$

⁴ cf. Section 3.5.

⁵ External parameters of A proper must be fixed at the partial differentiation for obtaining the internal energy of A with regard to the implied condition of the general expression Eq. (3.15).

$$U_A = kT^2 \left(\frac{\partial \log \mathcal{Q}A}{\partial T} \right)_\beta, \quad (3.47.A)$$

$$U_{K,\beta(0)} = kT^2 \frac{\partial \log \mathcal{Q}K_{\beta(0)}}{\partial T}. \quad (3.47.K)$$

Thermodynamical forms are obtained by simply rewriting expressions obtained in the previous section in terms of F 's and U 's as follows:

$$F = F_A + \sum_b \int_{\beta_b(0)}^{\beta_b} \Pi_{\beta_b}^A d\beta_b + F_{K,\beta(0)}, \quad (3.48)$$

$$\begin{aligned} -kT \log \lambda &= \Delta_\lambda F_A + \sum_b \Pi_{\beta_b}^A \Delta_\lambda \beta_b \\ &+ \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \Pi_{\beta_b}^A d\beta_b, \end{aligned} \quad (3.49)$$

$$\begin{aligned} U &= F - T \frac{\partial F}{\partial T} = U_A + \sum_b \int_{\beta_b(0)}^{\beta_b} \Pi_{\beta_b}^A d\beta_b \\ &- T \sum_b \int_{\beta_b(0)}^{\beta_b} \frac{\partial \Pi_{\beta_b}^A}{\partial T} d\beta_b + U_{K,\beta(0)}, \end{aligned} \quad (3.50)$$

$$\begin{aligned} kT^2 \frac{\partial \log \lambda}{\partial T} &= \Delta_\lambda U_A + \sum_b \Pi_{\beta_b}^A \Delta_\lambda \beta_b \\ &+ \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \Pi_{\beta_b}^A d\beta_b \\ &- T \sum_b \frac{\partial \Pi_{\beta_b}^A}{\partial T} \Delta_\lambda \beta_b \\ &- T \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \frac{\partial \Pi_{\beta_b}^A}{\partial T} d\beta_b. \end{aligned} \quad (3.51)$$

3.9. Thermodynamical form of λ 's and derived quantities for the assembly A_p

Thermodynamical form of $-kT \log \mathcal{Q}(A + K)$, $-kT \log \lambda$, $kT^2 (\partial \log \mathcal{Q}(A + K) / \partial T)$, and $kT^2 (\partial \log \lambda /$

δT) derived in the previous section with special reference to the assembly A correspond in general to no ready-made thermodynamical functions except when $\lambda \equiv p^\delta$ and $A \equiv A_P$ or when only external parameter of A is the volume V_A and the conjugated average force the pressure P_A is kept constant independent of V_A and T .

Thermodynamical form in the previous section are developed later with this particular case that $\beta \equiv V_A$, $\Pi^A \equiv P_A = \text{constant}$, and $\lambda \equiv p^\delta$ or $-RT \log \lambda = \mu^\delta$, first rewriting the expressions there as follows:

$$(3.17) \quad P_A = - \left(\frac{\partial F_A}{\partial V_A} \right)_T, \quad (3.52)$$

$$(3.48) \quad F = F_A + P_A V_A + F_{K,V_A=0}, \quad (3.53)$$

$$(3.49) \quad \mu^\delta = \bar{F}_A^\delta + P_A \bar{V}_A^\delta, \quad (3.54)$$

$$(3.50) \quad U = F - T \frac{\partial F}{\partial T} = U_A + P_A V_A + U_{K,V_A=0}, \quad (3.55)$$

$$(3.51) \quad \mu^\delta - T \frac{\partial \mu^\delta}{\partial T} = \bar{U}_A^\delta + P_A \bar{V}_A^\delta. \quad (3.56)$$

$F_{K,V_A=0}$ and $U_{K,V_A=0}$ give, respectively, particular values of $F_{K,\beta(0)}$ and $U_{K,\beta(0)}$ at $\beta(0) \equiv V_A(0) = 0$ and

$$\bar{F}_A^\delta = \Delta|_p F_A, \quad (3.57.F)$$

$$\bar{U}_A^\delta = \Delta|_p U_A, \quad (3.57.U)$$

$$\bar{V}_A^\delta = \Delta|_p V_A, \quad (3.57.V)$$

are partial molar quantities at the particular condition of A_p , i.e. at the constant pressure.

We see the variable part $F_A + P_A V_A$ of F in Eq. (3.53) correspond to Gibbs' free energy Z_A , that $U_A + P_A V_A$ of U in Eq. (3.55) to the enthalpy X_A , $\bar{F}_A^\delta + P_A \bar{V}_A^\delta$ of Eq. (3.54) to the partial molar quantity \bar{Z}_A^δ of Z_A and $\bar{U}_A^\delta + P_A \bar{V}_A^\delta$ of Eq. (3.56) to the partial molar enthalpy \bar{X}_A^δ of X_A , i.e.

$$Z_A = F_A + P_A V_A, \quad (3.58)$$

$$X_A = U_A + P_A V_A, \quad (3.59)$$

$$\bar{Z}_A^\delta = \bar{F}_A^\delta + P_A \bar{V}_A^\delta \quad (3.60)$$

and

$$\bar{X}_A^\delta = \bar{U}_A^\delta + P_A \bar{V}_A^\delta. \quad (3.61)$$

In term of these “ready-made” thermodynamical functions previous equations are, respectively, rewritten as follows:^{6,7}

$$(3.52) \quad \left(\frac{\partial Z_A}{\partial P_A} \right)_T = V_A, \quad (3.62)$$

$$(3.54) \quad \mu^\delta = \bar{Z}_A^\delta, \quad (3.63)$$

$$(3.55) \quad Z_A - T \frac{\partial Z_A}{\partial T} = X_A, \quad (3.64)$$

$$(3.56) \quad \mu^\delta - T \frac{\partial \mu^\delta}{\partial T} = \bar{X}_A^\delta. \quad (3.65)$$

Incorporating Eqs. (3.62) and (3.63), we have further

$$\left(\frac{\partial \mu^\delta}{\partial P_A^\delta} \right)_T = \bar{V}_A^\delta. \quad (3.66)$$

These relations are obtained in alternative forms by introducing the entropy S_A of the assembly A proper, according to Eq. (3.21), i.e.⁸

$$S_A = - \left(\frac{\partial F_A}{\partial T} \right)_{V_A}. \quad (3.67)$$

We have thus from Eq. (3.58)⁹

$$S_A = - \frac{\partial Z_A}{\partial T}, \quad (3.68)$$

⁶ Expressing $(\partial Z_A / \partial P_A)_T$ by differentiation of Eq. (3.58) in the form

$$\left(\frac{\partial Z_A}{\partial P_A} \right)_T = \left(\frac{\partial F_A}{\partial V_A} \right)_T \left(\frac{\partial V_A}{\partial P_A} \right)_T + P_A \left(\frac{\partial V_A}{\partial P_A} \right)_T + V_A,$$

we have Eq. (3.62) from Eq. (3.52).

⁷ Substituting F into Eq. (3.55) from Eq. (3.53) and observing Eqs. (3.58), (3.59) and the relation

$$F_{K,V_A=0} - T \frac{\partial F_{K,V_A=0}}{\partial T} = U_{K,V_A=0}$$

valid as a special case of Eq. (3.16) we have the above relation.

⁸ The external parameter of A proper, i.e. the volume must be kept constant at the partial differentiation with regard to the implied condition of the general expression Eq. (3.21).

⁹ According to the identity,

$$\left(\frac{\partial F_A}{\partial T} \right)_{P_A} = \left(\frac{\partial F_A}{\partial T} \right)_{V_A} + \left(\frac{\partial F_A}{\partial V_A} \right)_T \left(\frac{\partial V_A}{\partial T} \right)_{P_A}$$

and Eqs. (3.52), (3.58) and (3.67) we have above relation, where $(\partial Z_A / \partial T)_{P_A}$ is expressed without suffix.

from Eq. (3.64)

$$Z_A + TS_A = X_A, \quad (3.69)$$

from Eqs. (3.68) and (3.63)

$$\bar{S}_A^\delta = -\frac{\partial \mu^\delta}{\partial T}, \quad (3.70)$$

and from Eqs. (3.63) and (3.69)

$$\mu^\delta + T\bar{S}_A^\delta = \bar{X}_A^\delta, \quad (3.71)$$

where partial differential coefficients without suffix and the partial molar quantity \bar{S}_A^δ are all referred to the specified condition of A_P , i.e. to the constant pressure.

We rewrite these relations for partial molar quantities of A for the sake of later applications dropping the subscript A signifying instead explicitly the specified condition by suffix P ,

$$\mu^\delta = \bar{Z}_P^\delta, \quad (3.72.\mu)$$

$$\left(\frac{\partial \mu^\delta}{\partial T}\right)_P = -\bar{S}_P^\delta, \quad (3.72.S)$$

$$\mu^\delta = \bar{X}_P^\delta - T\bar{S}_P^\delta. \quad (3.72.E)$$

Corresponding relations for A_V of the assembly A , whose only external parameter V is fixed, may be written down as follows as the special case of those given in Section 3.4, signifying explicitly the constancy of the volume, i.e.

$$\mu^\delta = \bar{F}_V^\delta, \quad (3.73.\mu)$$

$$\left(\frac{\partial \mu^\delta}{\partial T}\right)_V = -\bar{S}_P^\delta, \quad (3.73.S)$$

and

$$\mu^\delta = \bar{U}_V^\delta - T\bar{S}_V^\delta. \quad (3.73.E)$$

The relation between two groups of partial molar quantities appearing, respectively, in Eqs. (3.72. μ), (3.72.S), (3.72.E), (3.73. μ), (3.73.S) and (3.73.E) is developed as follows.

It is immediately transposed from Eqs. (3.60), (3.61) and (3.66) that,

$$\bar{Z}_P^\delta = \bar{F}_P^\delta + P\bar{V}_P^\delta, \quad (3.74.Z)$$

$$\bar{X}_P^\delta = \bar{U}_P^\delta + P\bar{V}_P^\delta, \quad (3.74.X)$$

$$\left(\frac{\partial \mu^\delta}{\partial P}\right)_T = \bar{V}_P^\delta. \quad (3.74.V)$$

It follows on the other hand from the identity of p^δ or μ^δ of the assembly A_P with that of A_V as verified in Section 3.6 and according to Eqs. (3.72.E) and (3.73.E)

$$\mu^\delta = \bar{X}_P^\delta - T\bar{S}_P^\delta = \bar{U}_V^\delta - T\bar{S}_V^\delta. \quad (3.74.\mu)$$

We derive from Eq. (3.72.S)

$$\bar{S}_P^\delta = -\left(\frac{\partial \mu}{\partial T}\right)_P = -\left(\frac{\partial \mu}{\partial T}\right)_V + \left(\frac{\partial \mu}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

or according to Eqs. (3.73.S) and (3.74.V) and to the relation

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(1/V)(\partial V/\partial T)_P}{(1/V)(\partial V/\partial P)_T}, \quad (3.74.S)$$

$$\bar{S}_P^\delta = \bar{S}_V^\delta + \frac{\alpha}{\beta}\bar{V}_P^\delta,$$

where

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

are the expansion coefficient and the compressibility respectively.

From Eqs. (3.74.S), (3.74. μ) and (3.74.X) we have

$$\bar{X}_P^\delta = \bar{U}_V^\delta + T\frac{\alpha}{\beta}\bar{V}_P^\delta \quad (3.75.X)$$

and

$$\bar{U}_P^\delta = \bar{U}_V^\delta + \left(T\frac{\alpha}{\beta} - P\right)\bar{V}_P^\delta. \quad (3.75.U)$$

Finally, we derive from Eqs. (3.72.S), (3.74. μ) and (3.74.V)

$$\left(\frac{\partial \bar{X}_P^\delta}{\partial P}\right)_T = \bar{V}_P^\delta - T \left(\frac{\partial \bar{V}_P^\delta}{\partial T}\right)_P. \quad (3.76)$$

3.10. Statistical thermodynamics of homogeneous fluid

We call such an assembly or such a special part of an assembly a homogeneous fluid that only external parameter is volume and Q^δ of every constituent molecule is, respectively, constant all over the space, depending only on temperature, pressure and on the composition but not on its absolute magnitude.

A homogeneous fluid is called ideal solution with respect to certain components if Q^δ of the latters

are independent of any concentration of these components. The latter are called ideal components, the homogeneous fluid ideal with respect to the components and the homogeneous fluid consisting of remaining components the solvent. We may expect a homogeneous fluid is ideal with respect to a component which is dilute enough so that the work $-kT \log q_{\sigma}^{\delta}$ and hence Q^{δ} of every constituent is constant independent of the concentration of the dilute component.

A homogeneous fluid is called a perfect gas or simply a gas if the latter is ideal with respect to every component.

Following are deduced from the above definition.

Let an ideal solution A with respect to a component δ_0 be separated from its solvent B consisting of $\delta_1, \dots, \delta_s$ by a semipermeable membrane which is impermeable only to δ_0 . The whole assembly is considered as in equilibrium at a constant volume, and B big enough so that the shift of the membrane practically makes no difference in its pressure nor in composition.

Since Q^{δ} 's and hence μ^{δ} 's according to Eqs. (3.5) and (3.25) depend only on the pressure and composition but not on the absolute magnitude of the fluid at constant temperature, Gibbs' free energy Z of a homogeneous fluid is expressed according to Eq. (3.72.μ) in the form,

$$Z = \sum_i n^{\delta_i} \mu^{\delta_i}$$

and hence F according to Eq. (3.58)

$$F = \sum_i n^{\delta_i} \mu^{\delta_i} - PV, \quad (3.77)$$

where n^{δ_i} is the number of moles of δ_i .

The F of the part A or B is now, respectively, expressed as

$$F_A = n^{\delta_0} \mu^{\delta_0} + \sum_{i=1}^{i=s} n_A^{\delta_i} \mu_A^{\delta_i} - P_A V_A \quad \text{or}$$

$$F_B = n^{\delta_0} \mu^{\delta_0} + \sum_{i=1}^{i=s} n_B^{\delta_i} \mu_B^{\delta_i} - P_B V_B.$$

Because of the assumed equilibrium we have, however, according to Eqs. (3.6) and (3.25)

$$\mu_A^{\delta_i} = \mu_B^{\delta_i} = \mu^{\delta_i} = \text{constant}, \quad i = 1, \dots, s. \quad (3.78)$$

Denoting the sum $n_A^{\delta_i} + n_B^{\delta_i}$ by n^{δ_i} we have for F of the whole assembly

$$F = F_A + F_B = n^{\delta_0} \mu^{\delta_0} + \sum_i n^{\delta_i} \mu^{\delta_i} - P_A V_A - P_B V_B. \quad (3.79)$$

Differentiating F with respect to V_A we obtain the average force $\Pi^{\delta_0} = P_A - P_B$ conjugated with V_A or the osmotic pressure,

$$P_A - P_B = - \left(\frac{\partial F}{\partial V_A} \right)_T = -n^{\delta_0} \left(\frac{\partial \mu^{\delta_0}}{\partial V_A} \right)_T + P_A - P_B + V_A \left(\frac{\partial P_A}{\partial V_A} \right)_T$$

or

$$V_A \left(\frac{\partial P_A}{\partial V_A} \right)_T = n^{\delta_0} \left(\frac{\partial \mu^{\delta_0}}{\partial V_A} \right)_T \quad (3.80)$$

with regard to the relation that $V_A + V_B = \text{constant}$.

According to Eqs. (3.5) and (3.25) we have

$$\mu^{\delta} = \mu_1^{\delta} + RT \log N^{\delta} \quad (3.81)$$

where

$$\mu_1^{\delta} = -RT \log Q^{\delta} \quad (3.82)$$

and hence noting $N^{\delta_0} = n^{\delta_0} / V_A$,

$$\left(\frac{\partial \mu^{\delta_0}}{\partial V_A} \right)_T = \left(\frac{\partial \mu_1^{\delta_0}}{\partial P_A} \right)_T \left(\frac{\partial P_A}{\partial V_A} \right)_T - \frac{RT}{V_A} \quad (3.83)$$

inasmuch as Q^{δ} of the ideal component is the function only of pressure at a constant temperature. $(\partial \mu_1^{\delta_0} / \partial P_A)_T$ is obtained from Eq. (3.81) as

$$\left(\frac{\partial \mu^{\delta_0}}{\partial P_A} \right)_T = \bar{V}_P^{\delta_0} = \left(\frac{\partial \mu_1^{\delta_0}}{\partial P_A} \right)_T + RT \beta_A, \quad (3.84)$$

where

$$\beta_A = - \left(\frac{\partial \log V_A}{\partial P_A} \right)_T$$

is the compressibility.

By Eqs. (3.80), (3.83) and (3.84), we have

$$\left(\frac{\partial P_A}{\partial V_A} \right)_T = - \frac{n^{\delta_0} RT}{V_A (V_A - n^{\delta_0} \bar{V}_P^{\delta_0} + n^{\delta_0} RT \beta_A)},$$

or by integration, remembering that $\Pi^{\delta_0} = P_A - P_B$,

$$\Pi^{\delta_0} = n^{\delta_0} RT \int_{V_A}^{\infty} \frac{dV_A}{V_A(V_A - n^{\delta_0} \bar{V}_P^{\delta_0} + n^{\delta_0} RT \beta_A)}, \quad (3.85)$$

provided that $P_A = P_B$ at $V_A = \infty$.

If $n^{\delta_0} RT \beta_A$ is negligible compared with $V_A - n^{\delta_0} \bar{V}_P^{\delta_0}$ and $\bar{V}_P^{\delta_0}$ is constant independent of V_A , which might be the case for a colloidal solution, $n^{\delta_0} \bar{V}_P^{\delta_0}$ being the total displacement volume of the colloidal particles, Eq. (3.85) assumes the form with regard to the relation $N^{\delta_0} = n^{\delta_0}/V_A$,

$$\Pi^{\delta_0} = -\frac{RT}{\bar{V}_P^{\delta_0}} \log(1 - N^{\delta_0} \bar{V}_P^{\delta_0}). \quad (3.86)$$

Eq. (3.86) might be useful for the determination of the molecular weight of the colloidal particles by analysing the measurement of Π^{δ_0} at different concentrations, whereby the displacement volume $n^{\delta_0} \bar{V}_P^{\delta_0}$ is simultaneously determined.

If $n^{\delta_0} \bar{V}_P^{\delta_0} - n^{\delta_0} RT \beta_A$ is negligibly small compared with V_A , we have from Eq. (3.85)

$$\Pi^{\delta_0} = n^{\delta_0} \frac{RT}{V}. \quad (3.87)$$

If ideal components $\delta_0, \dots, \delta_t$ are confined together in the space A , we have by similar reasoning instead of Eq. (3.85)

$$\Pi = \sum_{i=0}^{i=t} n^{\delta_i} RT \int_{V_A}^{\infty} \frac{dV_A}{V_A \{V_A - \sum_{i=0}^{i=t} n^{\delta_i} (\bar{V}_P^{\delta_i} - RT \beta_A)\}}, \quad (3.88)$$

and instead of Eq. (3.87), if $\sum_{i=0}^{i=t} n^{\delta_i} (\bar{V}_P^{\delta_i} - RT \beta_A)$ is negligibly small compared with V_A ,

$$\Pi = \sum_{i=0}^{i=t} n^{\delta_i} \frac{RT}{V}. \quad (3.89)$$

In the further special case of a gas, when the assembly is ideal with respect to every component we have according to our definition that, $(\partial \mu_1^{\delta_0} / \partial P)_T = 0$, since the pressure varies nothing but the concentration of ideal components. We have hence according to Eq. (3.84),

$$RT \beta - \bar{V}_P^{\delta_i} = 0, \quad i = 1, \dots, s \quad (3.90)$$

or taking the fact thereby that $P_B = 0$ or $\Pi = P_A$ into account and dropping subscript A

$$PV = \sum_{i=0}^{i=s} n^{\delta_i} RT, \quad (3.91)$$

i.e. the ideal gas law. It may be noted that Eq. (3.90) is conversely satisfied by Eq. (3.91) inasmuch as $\beta = 1/P$ and $\bar{V}_P^{\delta_i} = RT/P$ according to the latter.

For a general homogeneous fluid we define $\bar{F}_{V,1}^{\delta}$, $\bar{F}_{P,1}^{\delta}$, and $\bar{Z}_{P,1}^{\delta}$, as

$$\bar{F}_{V,1}^{\delta} = \bar{F}_V^{\delta} - RT \log N^{\delta}, \quad (3.92.V)$$

$$\bar{F}_{P,1}^{\delta} = \bar{F}_P^{\delta} - RT \log N^{\delta}, \quad (3.92.P)$$

$$\bar{Z}_{P,1}^{\delta} = \bar{Z}_P^{\delta} - RT \log N^{\delta}. \quad (3.92.Z)$$

It follows immediately from Eqs. (3.72.μ), (3.73.μ), (3.74.Z), (3.81) and (3.82)

$$\mu_1^{\delta} = \bar{F}_{V,1}^{\delta} = \bar{F}_{P,1}^{\delta} + P \bar{V}_P^{\delta} = \bar{Z}_{P,1}^{\delta} \quad (3.93.μ)$$

and from Eqs. (3.74.V), (3.92) and (3.93.μ)

$$\left(\frac{\partial \bar{F}_{V,1}^{\delta}}{\partial P} \right)_T = \left(\frac{\partial \bar{Z}_{P,1}^{\delta}}{\partial P} \right)_T = \bar{V}_P^{\delta} - RT \beta, \quad (3.93.P)$$

remembering that,

$$N^{\delta} = \frac{n^{\delta}}{V}. \quad (3.93.N)$$

$\bar{S}_{V,1}^{\delta}$ and $\bar{S}_{P,1}^{\delta}$ are defined as follows:

$$\bar{S}_{V,1}^{\delta} = \bar{S}_V^{\delta} + R \log N^{\delta}, \quad (3.94.V)$$

$$\bar{S}_{P,1}^{\delta} = \bar{S}_P^{\delta} + R \log N^{\delta}. \quad (3.94.P)$$

We have on the other hand differentiating μ^{δ} of Eq. (3.81) with respect to T , respectively, with constant V or P

$$\left(\frac{\partial \mu^{\delta}}{\partial T} \right)_V = \left(\frac{\partial \mu_1^{\delta}}{\partial T} \right)_V + R \log N^{\delta}, \quad (3.95.V)$$

$$\left(\frac{\partial \mu^{\delta}}{\partial T} \right)_P = \left(\frac{\partial \mu_1^{\delta}}{\partial T} \right)_P - RT \alpha + R \log N^{\delta}. \quad (3.95.P)$$

It follows from Eqs. (3.72.S), (3.73.S), (3.94) and (3.95)

$$\bar{S}_{V,1}^{\delta} = - \left(\frac{\partial \mu_1^{\delta}}{\partial T} \right)_V, \quad (3.96.V)$$

$$\bar{S}_{P,1}^\delta = - \left(\frac{\partial \mu_1^\delta}{\partial T} \right)_P + RT\alpha \quad (3.96.P)$$

and from Eqs. (3.74.S) and (3.94)

$$\bar{S}_{P,1}^\delta = \bar{S}_{V,1}^\delta + \frac{\alpha}{\beta} \bar{V}_P^\delta. \quad (3.96.S)$$

$\bar{U}_{V,1}^\delta$, $\bar{U}_{P,1}^\delta$, and $\bar{X}_{P,1}^\delta$ are now defined as

$$\bar{U}_{V,1}^\delta = \bar{F}_{V,1}^\delta + T \bar{S}_{V,1}^\delta, \quad (3.97.U_V)$$

$$\bar{U}_{P,1}^\delta = \bar{X}_{P,1}^\delta + P \bar{V}_P^\delta, \quad (3.97.U_P)$$

$$\bar{X}_{P,1}^\delta = \bar{Z}_{P,1}^\delta + T \bar{S}_{P,1}^\delta, \quad (3.97.X_P)$$

along with the expressions, respectively, for \bar{U}_V^δ , \bar{U}_P^δ , and \bar{X}_P^δ as derived from Eqs. (3.72), (3.73) and (3.74), i.e.

$$\bar{U}_V^\delta = \bar{F}_V^\delta + T \bar{S}_V^\delta, \quad (3.98.U_V)$$

$$\bar{U}_P^\delta = \bar{X}_P^\delta - P \bar{V}_P^\delta, \quad (3.98.U_P)$$

$$\bar{X}_P^\delta = \bar{Z}_P^\delta + T \bar{S}_P^\delta. \quad (3.98.X_P)$$

It follows from Eqs. (3.92), (3.94), (3.97) and (3.98)

$$\bar{U}_{V,1}^\delta = \bar{U}_V^\delta, \quad (3.99.U_V)$$

$$\bar{U}_{P,1}^\delta = \bar{X}_P^\delta, \quad (3.99.U_P)$$

$$\bar{X}_{P,1}^\delta = \bar{U}_P^\delta \quad (3.99.X_P)$$

and hence from Eqs. (3.75), (3.76) and (3.99)

$$\bar{X}_{P,1}^\delta = \bar{U}_{V,1}^\delta + T \frac{\alpha}{\beta} \bar{V}_P^\delta, \quad (3.100.X)$$

$$\bar{U}_{P,1}^\delta = \bar{U}_{V,1}^\delta + \left(T \frac{\alpha}{\beta} - P \right) \bar{V}_P^\delta, \quad (3.100.U)$$

$$\left(\frac{\partial \bar{X}_{P,1}^\delta}{\partial P} \right)_T = \bar{V}_P^\delta - T \left(\frac{\partial \bar{V}_P^\delta}{\partial T} \right)_P. \quad (3.101)$$

In the case of ideal solution for which μ_1^δ is constant at constant T and P the above quantities with suffix 1 are all similarly constant independent of N^δ provided that α and β are constant or their shift with N^δ is negligible, as it follows from the above definitions and derived relations.¹⁰ It is usual to regard these quantities the properties of the standard state of the ideal

¹⁰ $\bar{F}_{V,1}^\delta$, $(\partial \bar{F}_{V,1}^\delta / \partial P)_T$ and hence \bar{V}_P^δ are constant according to Eq. (3.93.P) independent of N^δ . Hence, it follows from other relations the same is true with all quantities suffixed with 1.

solution where $N^\delta = 1$. Here we should rather treat these quantities as the properties of our homogeneous solution itself, if ideal or not, than have recourse to the standard state.

In the case of a gas, the independency of α , β and hence of \bar{V}_P^δ is strictly secured with the following particular values as derived from Eq. (3.91),

$$\alpha = \frac{1}{T}, \quad (3.102.\alpha)$$

$$\beta = \frac{1}{P}, \quad (3.102.\beta)$$

$$\bar{V}_P^\delta = \frac{RT}{P}. \quad (3.102.V)$$

Eqs. (3.93), (3.96), (3.97), (3.100) and (3.101) now assume the particular forms:

$$\mu_1^\delta = \bar{F}_{V,1}^\delta = \bar{F}_{P,1}^\delta + RT = \bar{Z}_{P,1}^\delta \quad (3.103.\mu)$$

$$\bar{S}_{V,1}^\delta = - \left(\frac{\partial \mu_1^\delta}{\partial T} \right)_V = \bar{S}_{P,1}^\delta - R = - \left(\frac{\partial \mu_1^\delta}{\partial T} \right)_P \quad (3.103.S)$$

$$\bar{U}_{V,1}^\delta = \bar{U}_{P,1}^\delta = \bar{X}_{P,1}^\delta - RT \quad (3.103.U)$$

$$\left(\frac{\partial \bar{X}_{P,1}^\delta}{\partial P} \right)_P = 0 \quad (3.103.X)$$

4. Application-I. Equilibrium

4.1. Bose–Einstein and Fermi–Dirac statistics

Assuming both Bose–Einstein and Fermi–Dirac gas are as a whole describable by an appropriate petit quantum canonical ensemble, the mean population or the distribution function f_s of quantum state σ_s of energy ε_s for individual molecules δ 's is given by

$$f_s = \frac{(0 \times \Theta_{\sigma_s(0)}) + (1 \times \Theta_{\sigma_s(\delta)}) + (2 \times \Theta_{\sigma_s(2\delta)}) + (3 \times \Theta_{\sigma_s(3\delta)}) + \dots}{\Theta_{\sigma_s(0)} + \Theta_{\sigma_s(\delta)} + \Theta_{\sigma_s(2\delta)} + \Theta_{\sigma_s(3\delta)} + \dots}, \quad (4.1)$$

where $\Theta_{\sigma_s(\nu\delta)}$ denotes the probability that ν pieces of δ 's simultaneously occupy the elementary state σ_s , which vanishes for $\nu > 1$ according to the Pauli principle in the case of Fermi–Dirac gas.

$\Theta_{\sigma_s(\nu\delta)}$ in the case of Bose–Einstein gas may be written according to the definitions Eqs. (2.4) and (2.5)

$$\Theta_{\sigma_s(\nu\delta)} = \frac{\mathcal{Q}C_{\sigma_s(0)}}{\mathcal{Q}C_0} \frac{\mathcal{Q}C_{\sigma_s(\nu\delta)}}{\mathcal{Q}C_{\sigma_s(0)}} = \Theta_{\sigma_s(0)} \frac{(\mathcal{Q}C_{\sigma_s(\delta)}^\delta / \mathcal{Q}C_{\sigma_s(0)}) \cdots (\mathcal{Q}C_{\sigma_s(\nu\delta)}^{\nu\delta} / \mathcal{Q}C_{\sigma_s((\nu-1)\delta)}^{(\nu-1)\delta})}{(\mathcal{Q}C_{\sigma_s(\nu\delta)}^{\nu\delta} / \mathcal{Q}C_{\sigma_s(\nu\delta)}^{(\nu-1)\delta}) \cdots (\mathcal{Q}C_{\sigma_s(\nu\delta)}^\delta / \mathcal{Q}C_{\sigma_s(\nu\delta)}^\delta)} \quad (4.2)$$

The denominator of the third member of Eq. (4.2) simply equals $(p^\delta)^\nu$ according to the approximation of Section 2.4, provided that ν is not very large.

The first factor of the numerator equals $q_{\sigma_s}^\delta$ according to Eq. (2.3), i.e.

$$q_{\sigma_s}^\delta = \frac{\mathcal{Q}C_{\sigma_s}^\delta(\sigma)}{\mathcal{Q}C_{\sigma_s(0)}} \quad (4.3)$$

which may be evaluated as follows: Since Bose–Einstein statistics attributes the same statistical weight to every possible distribution of N molecules in the gas over all elementary states and to the total energy, the sum $\sum_t \nu_t \varepsilon_t$ of individual energies ε_t 's of all molecules, respectively, at quantum states σ_t 's, $\mathcal{Q}C_{\sigma_s(0)}$ is the summation of Boltzmann factors of $\sum_t \nu_t \varepsilon_t$ over all possible distribution of N molecules with the constraint $\nu_s = 0$, i.e. that of N molecules over all σ_t 's except σ_s . $\mathcal{Q}C_{\sigma_s(\delta)}^\delta$ is similarly that of $N + 1$ molecules with the constraint $\nu_s = 1$ or that of N molecules over all σ_t 's except σ_s which holds $(N + 1)\delta$. It follows that there is one to one correspondence between Boltzmann factors of the two series relevant, respectively, to $\mathcal{Q}C_{\sigma_s(\delta)}^\delta$ and to $\mathcal{Q}C_{\sigma_s(0)}$ so that every one of the former series differs from the corresponding one of the latter by a factor $e^{-\varepsilon_s/kT}$. We have thus

$$\mathcal{Q}C_{\sigma_s(\delta)}^\delta = \mathcal{Q}C_{\sigma_s(0)} e^{-\varepsilon_s kT}, \quad (4.4)$$

or according to Eq. (4.3),

$$q_{\sigma_s}^\delta = e^{-\varepsilon_s/kT}. \quad (4.5)$$

It is shown similarly the remaining factors of the numerator equals $q_{\sigma_s}^\delta$ or $e^{-\varepsilon_s/kT}$ so far as the premise of the Bose–Einstein statistics goes.

We have hence in place of Eq. (4.2),

$$\Theta_{\sigma_s(\nu\delta)} = \left(\frac{q_{\sigma_s}^\delta}{p^\delta} \right)^\nu \Theta_{\sigma_s(0)}, \quad (4.6)$$

or substituting $\Theta_{\sigma_s(\nu\delta)}$ from Eq. (4.6) into Eq. (4.1),

$$f_s = \frac{(0 \times 1) + (1 \times (q_{\sigma_s}^\delta / p^\delta)) + (2 \times (q_{\sigma_s}^\delta / p^\delta)^2) + \cdots}{1 + (q_{\sigma_s}^\delta / p^\delta) + (q_{\sigma_s}^\delta / p^\delta)^2 + \cdots}. \quad (4.7)$$

Owing to the above approximation f_s is given by Eq. (4.7) only when the power series of the numerator and denominator converges or $(q_{\sigma_s}^\delta / p^\delta)^\nu$ for large ν is insignificant. In that case when $q_{\sigma_s}^\delta / p^\delta < 1$ Eq. (4.7) is written in the form,

$$f_s = \frac{q_{\sigma_s}^\delta / p^\delta}{1 - q_{\sigma_s}^\delta / p^\delta}$$

or expressing $q_{\sigma_s}^\delta$ by Eq. (4.5) and p^δ by the corresponding reversible work $\bar{\varepsilon} = -kT \log p^\delta$,

$$f_s = (e^{(\varepsilon_s - \bar{\varepsilon})/kT} - 1)^{-1}. \quad (4.8)$$

Remembering, on the other hand, that $\Theta_{\sigma_s(\nu\delta)} = 0$ for $\nu > 1$ in the case of Fermi–Dirac gas, we arrive, by a similar reasoning but without resorting to the approximation as above, at the distribution function,

$$f_s = (e^{(\varepsilon_s - \bar{\varepsilon})/kT} + 1)^{-1}.$$

4.2. Homogeneous equilibrium

The equilibrium relation Eq. (3.7) readily affords the equation,

$$\prod^a \left(\frac{\mathcal{Q}_{\delta_a^A}}{N_{\delta_a^A}} \right)^{\nu_a^A} = \prod^b \left(\frac{\mathcal{Q}_{\delta_b^B}}{N_{\delta_b^B}} \right)^{\nu_b^B} \quad (4.9)$$

for the equilibrium between two sets of components,

$$\delta^A = \sum_a \nu_a^A \delta_a^A \quad \text{and} \quad \delta^B = \sum_b \nu_b^B \delta_b^B$$

in a homogeneous fluid by substituting p^δ from Eq. (3.5), or

$$K_N = \frac{\prod^b (N_{\delta_b^B})^{\nu_b^B}}{\prod^a (N_{\delta_a^A})^{\nu_a^A}} = \frac{\prod^b (\mathcal{Q}_{\delta_b^B})^{\nu_b^B}}{\prod^a (\mathcal{Q}_{\delta_a^A})^{\nu_a^A}}, \quad (4.10)$$

where K_N is a constant independent of N^{δ_a} 's or the equilibrium constant provided that δ_a^A 's are all ideal components¹¹.

4.3. Heterogeneous equilibrium-1

We treat in this section the simplest case of heterogeneous equilibrium, i.e. the equilibrium between molecules of one kind adsorbed each on one of identical sites on a crystal surface and the molecules of the same kind in a homogeneous fluid. Our model of the crystal surface consists in general of small segments of lattice planes, each lattice point or a certain set of lattice points on any one of them providing a site σ^A for an adsorbed molecule where Q^δ or N^δ in Eq. (3.5) is concentrated, each segment being however big enough so that geometrically congruent σ^A 's on that segment are practically physically identical.

Because of the equilibrium we have according to Eq. (3.7)

$$p^{\delta_a} = p^{\delta_h},$$

where δ_a or δ_h denotes adsorbed molecule or that in the homogeneous fluid, respectively. Expressing p^{δ_a} by Eq. (3.1) and p^{δ_h} by Eq. (3.5), we have, dropping subscripts a and h ,

$$\frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(0)}} = q_\sigma^\delta \frac{N^\delta}{Q^\delta}. \quad (4.11)$$

If any site is either occupied by δ_a or else evacuated with certainty, we have¹²

$$\theta = \Theta_{\sigma(\delta)} = 1 - \Theta_{\sigma(0)}, \quad (4.12)$$

where θ is the degree of adsorption identified with $\Theta_{\sigma(\delta)}$.

Eliminating $\Theta_{\sigma(\delta)}$ and $\Theta_{\sigma(0)}$ from Eqs. (4.11) and (4.12), we have

$$\frac{\theta}{1 - \theta} = \frac{q_\sigma^\delta}{Q^\delta} N^\delta. \quad (4.13)$$

Introducing a further approximation that each molecule adsorbed on a site behaves like that in the homogeneous fluid in a cavity of the magnitude $|\sigma|$,

within which the potential energy being constantly lower than that in the homogeneous fluid by ε_σ , we have by similar reasoning as in the case of Eq. (3.4),

$$q_\sigma^\delta = |\sigma| Q^\delta e^{-\varepsilon_\sigma/kT}. \quad (4.14)$$

Substituting the above expression in Eq. (4.13) the latter assumes a more familiar form,

$$\frac{\theta}{1 - \theta} = |\sigma| e^{-\varepsilon_\sigma/kT} N^\delta, \quad (4.15)$$

which gives the Langmuir's adsorption isotherm.

4.4. Heterogeneous equilibrium-2

We proceed in this section to a bit more complicated case when δ in the homogeneous fluid splits, when adsorbed, into two parts δ_1 's each occupying a site as an adsorbed molecule in the foregoing example. The equilibrium relation Eq. (3.7) is now

$$p^\delta = (p^{\delta_1})^2$$

which gives, when p^δ and p^{δ_1} are substituted, respectively, from Eqs. (3.5) and (3.1), the relation

$$\frac{\Theta_{\sigma(0)}}{\Theta_{\sigma(\delta)}} q_\sigma^\delta = \sqrt{\frac{Q^\delta}{N^\delta}}. \quad (4.16)$$

Eliminating $\Theta_{\sigma(0)}$ and $\Theta_{\sigma(\delta)}$ from Eq. (4.12) and (4.16) as in the foregoing section, we have,

$$\frac{1 - \theta}{\theta} = \sqrt{\frac{Q^\delta}{N^\delta}}. \quad (4.17)$$

4.5. Heterogeneous equilibrium-3

In this section, we treat another case, when any one of identical sites is either vacant or occupied by any one of molecules of the several components of a homogeneous fluid.

We have immediately

$$\Theta_{\sigma(0)} + \sum_i \Theta_{\sigma(\delta_i)} = 1, \quad (4.18)$$

whereas for individual δ_i similarly as in the case of Eq. (4.11)

$$\frac{\Theta_{\sigma(\delta_i)}}{\Theta_{\sigma(0)}} = q_{\sigma}^{\delta_i} \frac{N^{\delta_i}}{Q^{\delta_i}} \quad (4.19)$$

¹¹ See Section 3.10.

¹² This can not be the case when δ is allowed to occupy any site which partly overlaps with σ .

and henceforth from Eqs. (4.18) and (4.19),

$$\theta_i = \Theta_{\sigma(\delta_i)} = \frac{q_{\sigma}^{\delta_i} N^{\delta_i} / Q^{\delta_i}}{1 + \sum_i q_{\sigma}^{\delta_i} N^{\delta_i} / Q^{\delta_i}}, \quad (4.20)$$

where θ_i is the degree of adsorption of i th component identified with $\Theta_{\sigma(\delta_i)}$.

Substituting the approximate expression for $q_{\sigma}^{\delta_i}$ from Eq. (4.14) we have Eq. (4.20) in the form,

$$\theta_i = \frac{|\sigma| N^{\delta_i} e^{-\varepsilon_{\sigma_i}/kT}}{1 + \sum_i |\sigma| N^{\delta_i} e^{-\varepsilon_{\sigma_i}/kT}}, \quad (4.21)$$

where ε_{σ_i} is ε_{σ} for δ_i . An expression identical with Eq. (4.21) is arrived at by Hückel [5] by a special reasoning.

4.6. Heterogeneous equilibrium-4

In this section, we develop a method of deriving the adsorption isotherm allowing for the mutual interaction among adsorbed molecules.

Our method will first be exemplified with the case when the molecules δ 's of only one kind from a homogeneous fluid are adsorbed in equilibrium each on one of the identical sites σ 's allayed on a plane square pattern, the interaction being significant only between directly neighboring adsorbed molecules.

We denote our assembly, consisting of the adsorbent attached with a definite number of δ 's and the homogeneous fluid, by C with appropriate subscripts: $C_{\sigma_0(0)}$ or $C_{\sigma_0(\delta)}$ thus denotes that with its particular site σ_0 evacuated or occupied, respectively, $C_{\sigma_s(0)}$ or $C_{\sigma_s(\delta)}$ that with σ_s , one of four direct neighbors of σ_0 numbered by $s = 1, 2, 3$ or 4 , evacuated or occupied, respectively, $C_{\Sigma(0)}$ that with the set of all five sites σ_0 and σ_s 's denoted by Σ , are evacuated, and finally C_0 that without any such constraint.

QC_0 is now expressed in terms of $C_{\Sigma(0)}$, p^{δ} , $q_{\sigma,0}^{\delta}$, ξ , and η , the latter two as described later taking care of the mutual interaction, as

$$QC_0 = C Q_{\Sigma(0)} \sum_{t_0, \dots, t_4} \left(\frac{q_{\sigma,0}^{\delta}}{p^{\delta}} \right)^{t_0 + \dots + t_4} \times \xi^{t_0(t_1 + \dots + t_4)} \eta^{t_1 + \dots + t_4}, \quad (4.22)$$

where t_0 , etc. denote, respectively, 1 or 0, according as σ_0 , etc. is occupied or not, \sum_{t_0, \dots, t_4} the summation over all possible sets of values of t_0 , etc.

We see with regard to Eq. (4.22) that $q_{\sigma,0}^{\delta}/p^{\delta}$ would give the factor of multiplication of Zs when one of δ is picked up from outside and planted on any vacant site of Σ , and hence $\sum_{t_0, \dots, t_4} (q_{\sigma,0}^{\delta}/p^{\delta})^{t_0 + \dots + t_4}$ the factor to be multiplied to $QC_{\Sigma(0)}$ for making up QC_0 if the mutual interaction were absent. The factor ξ or η gives now the extra factor of multiplication either due to the interaction of each adjacent pair of adsorbed molecules inside Σ , or due to the interaction between one of them and others outside Σ , respectively. They may differ from unity except for σ_0 and is the same for $\sigma_1, \sigma_2, \sigma_3$ and σ_4 because of the symmetry of Σ . Carrying out the summation we have

$$QC_0 = QC_{\Sigma(0)} \left(1 + \frac{q_{\sigma,0}^{\delta} \eta}{p^{\delta}} \right)^4 + QC_{\Sigma(0)} \frac{q_{\sigma,0}^{\delta}}{p^{\delta}} \left(1 + \frac{q_{\sigma,0}^{\delta} \eta \xi}{p^{\delta}} \right)^4. \quad (4.23)$$

$QC_{\sigma_0(0)}$ or $QC_{\sigma_0(\delta)}$ is given, respectively, by the first or the second term on the right-hand side of Eq. (4.23), which is the part of the summation of Eq. (4.22), respectively, corresponding to $t_0 = 0$ or $t_0 = 1$, i.e.

$$QC_{\sigma_0(0)} = QC_{\Sigma(0)} \left(1 + \frac{q_{\sigma,0}^{\delta} \eta}{p^{\delta}} \right)^4, \quad (4.24)$$

$$QC_{\sigma_0(\delta)} = QC_{\Sigma(0)} \frac{q_{\sigma,0}^{\delta}}{p^{\delta}} \left(1 + \frac{q_{\sigma,0}^{\delta} \eta \xi}{p^{\delta}} \right)^4. \quad (4.25)$$

$QC_{\sigma_s(0)}$ is given as the part of the sum corresponding to $t_s = 0$ as

$$QC_{\sigma_s(0)} = QC_{\Sigma(0)} \times \left\{ \left(1 + \frac{q_{\sigma,0}^{\delta} \eta}{p^{\delta}} \right)^3 + \frac{q_{\sigma,0}^{\delta}}{p^{\delta}} \left(1 + \frac{q_{\sigma,0}^{\delta} \eta \xi}{p^{\delta}} \right)^3 \right\}. \quad (4.26)$$

The degree of adsorption θ or $\Theta_{\sigma_0(\delta)}$ is now given according to Eqs. (2.4), (4.23) and (4.25) in the form,

$$\theta = \Theta_{\sigma_0(\delta)} = \frac{(q_{\sigma,0}^{\delta}/p^{\delta})(1 + q_{\sigma,0}^{\delta} \eta \xi / p^{\delta})^4}{(q_{\sigma,0}^{\delta}/p^{\delta})(1 + q_{\sigma,0}^{\delta} \eta \xi / p^{\delta})^4 + (1 + q_{\sigma,0}^{\delta} \eta / p^{\delta})^4}. \quad (4.27)$$

We now deduce in accordance with Bethe [6] and Peierls [7] that $QC_{\sigma_0(0)}$ must equal $QC_{\sigma_s(0)}$, since σ_0 and σ_s are physically identical, i.e. according to Eqs. (4.24) and (4.26)

$$\left(1 + \frac{q_{\sigma,0}^\delta \eta}{p^\delta}\right)^4 = \left(1 + \frac{q_{\sigma,0}^\delta \eta}{p^\delta}\right)^3 + \frac{q_{\sigma,0}^\delta}{p^\delta} \left(1 + \frac{q_{\sigma,0}^\delta \eta \xi}{p^\delta}\right)^3. \quad (4.28)$$

Eliminating η from Eqs. (4.27) and (4.28) we have θ as a function of p^δ , $q_{\sigma,0}^\delta$ and ξ .

The p^δ is given by the equilibrium relation as in Sections 4.3 and 4.4 as the function of the concentration or pressure in the homogeneous fluid. The $q_{\sigma,0}^\delta$ is according to the definition given as the ratio of QM_σ^δ to QM , where M_σ^δ is the adsorbent in the fluid with only one δ adsorbed at σ and M the latter without adsorbed δ .

With the approximation that the δ and the rest of the assembly are each at thermal motion reciprocally in the mean potential field of the other and that the height of energy levels of M proper above the energy at rest remain unchanged by adsorbing δ , QM_σ^δ may be expressed by factors as

$$QM_\sigma^\delta = QM e^{-\varepsilon_0/kT} Q\delta$$

and hence we have for $q_{\sigma,0}^\delta$

$$q_{\sigma,0}^\delta = \frac{QM_\sigma^\delta}{QM} = e^{-\varepsilon_0/kT} Q\delta, \quad (4.29)$$

where $Q\delta$ is the Zs of δ moving in the mean potential field of M or the sum of Boltzmann factors of Eigenwerts referred to the minimum ε_0 of the mean potential.

The factor ξ is estimated again with the approximation that each of the two adsorbed molecules interacting moves reciprocally in the mean potential field of the other, the height of individual energy levels above the minimum potential energy remaining unaffected by the interaction. The interaction contributes thus simply a constant term u to the Eigenwerts of the whole assembly or a constant factor $\xi = e^{-u/kT}$ to the Zs. The ξ may thus be obtained by evaluating u properly.

Okamoto, Horiuti and Hirota [1] estimated $q_{\sigma,0}^\delta$ and ξ after this manner in developing their theory of the hydrogen electrode process.

The present method may readily be extended to the case when the pattern of sites is of less symmetry and the allowance is made for the interaction between remoter molecules than directly neighboring. Attributing different extra factor of multiplication η to every symmetry class of σ_s 's appropriate to respective symmetry operation with respect to Σ and different ξ to every pair of sites of different relative position in Σ , QC_0 , $QC_{\sigma_s(0)}$, $QC_{\sigma_0(0)}$ and $QC_{\sigma_0(\delta)}$ are given by $QC_{\Sigma(0)}$ multiplied by a function of p^δ , $q_{\sigma,0}^\delta$, η 's and ξ 's.

The degree of adsorption θ is given as in the previous cases by $QC_{\sigma_0(\delta)}/QC_0$ which is expressed in terms of $q_{\sigma,0}^\delta$, p^δ , η 's and ξ 's. But since we have so many different expressions for $QC_{\sigma_s(0)}$ as the number g of symmetry classes of σ_s 's as well as $QC_{\sigma_0(0)}$ which are to be set equal to each other, we have g independent relations among μ 's, p^δ , $q_{\sigma,0}^\delta$ and ξ 's. Solving η 's therefrom and substituting the latter into the expression for θ , we have θ in terms of p^δ , $q_{\sigma,0}^\delta$ and ξ 's. Since p^δ is in turn determined by the equilibrium relation, we obtain estimating $q_{\sigma,0}^\delta$ and ξ 's properly as in the previous case, θ as a function of the concentration of molecules in the homogeneous fluid, i.e. the adsorption isotherm.

An actual calculation by the method outlined above will be presented in later papers.

5. Application-II. Chemical reaction in general

5.1. The scope and procedure of application

At the present stage of the chemical kinetics a reaction is taken as the overall result of a sequence of elementary reactions, the sequence, which adequately describes the experimental result in conformity with the stoichiometrical relation or the chemical equation, being called its mechanism. According to the postulate is our procedure now the statistical mechanical description of the individual elementary reactions and hence of the overall rate synthesizing the latters.

Another postulate underlying to the current procedure in the chemical kinetics is that the rate of elementary reactions is determined at a given temperature and

external parameters solely by the momentary chemical composition of the assembly involved not depending on the history or explicitly on time. We might advance amplifying the latter a postulate in its place in detailed statistical mechanical terms thus affording an exact basis for the application of our procedure.

Consider an assembly which would be derived from the observed one if left standing under the prescribed external condition to attain an equilibrium. The elementary reaction will be there going on in either direction more or less fluctuating the chemical composition.

The canonical ensemble of the assembly at equilibrium will of course consist of overwhelming majority of examples of the chemical composition close to the average at equilibrium, but a few, if exceptional, will have the chemical composition of the observed assembly, where so-called irreversible reaction is in general in progress. We postulate now that the chance with which a particular elementary reaction occurs to the assembly as well as its momentary properties is given as the average over that part of the ensemble which happened to have the momentary chemical composition of the assembly.

We call the assembly in thermal equilibrium if thus describable and the corresponding part of Zs that of the assembly. In terms of the Zs we define λ 's of the assembly just as in the case of those in complete equilibrium. Taking the fixed chemical composition as the microscopic constraint the whole theory of λ developed in Section 3 is applicable for the assembly at thermal equilibrium.

After we have defined in the next section the reaction of the particular type we are going to deal with, we advance in Section 5.3 the expression for the rate of the elementary reaction at thermal equilibrium derived on the basis of the above postulate.

The overall chemical reaction to be composed of elementary reactions is generally expressed by

$$\delta^L = \delta^R, \quad (5.1)$$

where δ^L or δ^R denotes reactant or resultant consisting generally of each ν_i^L pieces of δ_i^L or of each ν_r^R pieces of δ_r^R , so that

$$\delta^L = \sum_i \nu_i^L \delta_i^L, \quad (5.2.L)$$

$$\delta^R = \sum_r \nu_r^R \delta_r^R. \quad (5.2.R)$$

We call, on the other hand, the set of elementary particles involved in the elementary reaction generally the reaction complex and that at the state before or after the elementary reaction in particular the initial or final complex in distinction, respectively, from the reactant or resultant of the overall reaction. The initial and the final complex are in general taken as consisting, respectively, of each ν_i^I pieces of molecules δ_i^I and each ν_f^F ones of δ_f^F that

$$\delta^I = \sum_i \nu_i^I \delta_i^I, \quad (5.3.I)$$

$$\delta^F = \sum_f \nu_f^F \delta_f^F. \quad (5.3.F)$$

The simplest mechanism is that of the reaction consisting of only one elementary reaction. The reaction of this mechanism will be called the simple reaction. In general, however, the sequence needs not even be a consecutive one but branched, multiple one so that several different courses are available for a reactant to pass into the resultant. The type of sequences or the mechanism of the reaction going to be dealt with is that, inclusive of the simple reaction, of the steady reaction with a rate-determining step proceeding at thermal equilibrium.

In Section 5.4, we express the rate in terms of λ 's. The expression is now ready for various particular applications in later sections.

5.2. The steady reaction with rate-determining step at thermal equilibrium

It is meant by steady reaction such one as that the rates of creation and consumption of every intermediate product are practically balanced and by the rate-determining step an elementary reaction which is necessary for the reaction to proceed at all and has a negligibly small rate in either direction compared with that of any other constituent elementary reaction of the reaction.

The following may be inferred from thus detailed definition.

- (i) The initial complex of the rate-determining step of the reaction is most probably transferred into the reactant rather than into the final complex, and the final complex into the resultant rather than into

the reactant or in other word that an initial complex of the rate-determining step originates practically all in the reactant and the final complex practically certainly pass into the resultant, and hence that one act of the rate-determining step is necessary and sufficient for the reaction complex of the rate-determining step to complete the reaction, i.e. to pass from the state of the reactant to that of the resultant.

- (ii) The excess of the rate of any elementary reaction in one direction over that in the reversed direction must be equal to or smaller¹³ than that of the rate-determining step for the reaction to proceed steadily or without accumulation of the intermediate product. But since the rate in either direction of the rate-determining step itself is negligible compared with either of any other elementary reaction, the same must be true with the excess. It follows that for any other elementary reaction than the rate-determining one the excess is negligibly small compared with its rate in either direction, or in other word both the rates are practically balanced.

5.3. The rate of the elementary reaction

The rate of elementary reaction which proceeds adiabatically inside an assembly at thermal equilibrium is derived as follows [8,9]:

$$\bar{v} = \kappa \frac{kT}{h} \frac{QC_0^{\delta^*}}{QC_0^{\delta^I}} \quad (5.4)$$

The $QC_0^{\delta^*}$ or $QC_0^{\delta^I}$ is the classical approximation of the Zs of the assembly $C_0^{\delta^*}$ or $C_0^{\delta^I}$, i.e. of the assembly C_0 of definite chemical composition augmented by the critical complex δ^* or by the initial complex δ^I .

$C_0^{\delta^*}$ is defined as $C_0^{\bar{\delta}}$ at a particular configuration corresponding to the minimum of $QC_0^{\bar{\delta}}$, where $C_0^{\bar{\delta}}$ is an assembly consisting of C_0 of definite chemical composition and the reaction complex $\bar{\delta}$ within the latter with its representative point in the configuration space resting on a hypersurface separating the region corresponding to the state of δ^I of $\bar{\delta}$ from that δ^F . The hypersurface thus determined is called the critical sur-

face and $\bar{\delta}$ at the corresponding particular state the critical complex δ^* .

The transmission coefficient κ in Eq. (5.4) is defined as follows: we consider the representative points of the part of canonical ensemble, referred to in Section 5.2, appropriate to the chemical composition of the assembly $C_0^{\bar{\delta}}$. Because of the microscopic reversibility, however, the flow of the representative points through the critical surface is blanced by the reversed one. The transmission coefficient κ is now the ratio of the number of representative points which complete the elementary reaction over that which transit the critical surface in either direction. It follows from the definition of $QC_0^{\delta^*}$ and κ the latters are the same for the reverse elementary reaction. The rate \tilde{v} of the reverse elementary reaction is hence given by

$$\tilde{v} = \kappa \frac{kT}{h} \frac{QC_0^{\delta^*}}{QC_0^{\delta^F}} \quad (5.5)$$

The derivation of the above expression has nothing to do with some equilibrium relation between the initial and the critical complex and is generally applicable to the assembly at thermal equilibrium not being restricted to the case of the reaction complex behaving dynamically independent. Nor it presupposes the existence of the saddle point of the potential energy and its being determinant of the rate. As shown later the expression thus derived includes that of Eyring [10] or of Evans and Polanyi [11] as its special case.

5.4. Classification of reaction and different expressions for the rate

Eqs. (5.4) and (5.5) for the rate of the elementary reaction may readily expressed according to Eq. (2.2) in terms of λ 's, i.e.

$$\bar{v} = \kappa \frac{kT}{h} \frac{p^{\delta^*}}{p^{\delta^I}}, \quad (5.6a)$$

$$\tilde{v} = \kappa \frac{kT}{h} \frac{p^{\delta^*}}{p^{\delta^F}} \quad (5.6b)$$

where

$$p^{\delta^I} = \prod_i (p^{\delta^I}_i)^{v_i^I}, \quad (5.7.1)$$

$$p^{\delta^F} = \prod_f (p^{\delta^F}_f)^{v_f^F} \quad (5.7.F)$$

¹³ The excess may be smaller than that of the rate-determining step when the course is branched.

according to Eqs. (2.11), (5.3.I) and (5.3.F). The function p^{δ^*} in Eqs. (5.6a) and (5.6b) may either be expressed according to Eq. (3.1) in the form,

$$p^{\delta^*} = \frac{\Theta_{\sigma^*(0)}}{\Theta_{\sigma^*(\delta)}} q_{\sigma^*}^{\delta^*} \quad (5.8)$$

or according to Eqs. (3.3) and (3.5) in the form,

$$p^{\delta^*} = \frac{Q^{\delta^*}}{N^{\delta^*}}, \quad (5.9)$$

where

$$Q^{\delta^*} = \lim_{|\sigma^*| \rightarrow 0} \frac{q_{\sigma^*}^{\delta^*}}{|\sigma^*|} \quad (5.10)$$

and σ^* denotes a small cavity of molecular dimension housing the centre of gravity of δ^* within. Substituting p^{δ^*} from Eq. (5.8) or from Eq. (5.9) into Eq. (5.6a) and (5.6b), we have

$$\vec{v} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{N^{\delta^*} p^{\delta^*}}, \quad (5.11a)$$

$$\tilde{v} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{N^{\delta^*} p^{\delta^* F}}, \quad (5.11b)$$

or

$$\vec{v} = \kappa \frac{kT}{h} \frac{\Theta_{\sigma^*(0)} q_{\sigma^*}^{\delta^*}}{\Theta_{\sigma^*(\delta^*)} p^{\delta^* I}}, \quad (5.12a)$$

$$\tilde{v} = \kappa \frac{kT}{h} \frac{\Theta_{\sigma^*(0)} q_{\sigma^*}^{\delta^*}}{\Theta_{\sigma^*(\delta^*)} p^{\delta^* F}}. \quad (5.12b)$$

We call along with Section 3.10 an elementary reaction homogeneous, if Q^{δ^*} and hence N^{δ^*} remain constant all over the space concerned, or heterogeneous, if Q^{δ^*} and hence N^{δ^*} are concentrated at site σ^* of the similar description as that of σ^A in Section 4.3. A reaction will be called homogeneous or heterogeneous according as its rate-determining step either.

Eq. (5.11) may conveniently be transformed as follows for the homogeneous elementary reaction. N^{δ^*} being the concentration of only one δ^* existing in the assembly,¹⁴ it may be identified with the reciprocal of volume V of the homogeneous fluid where δ^* is in. We obtain thus from Eq. (5.11),

$$\vec{v}_1 = \frac{\vec{v}}{V} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{p^{\delta^* I}}, \quad (5.13a)$$

$$\tilde{v}_1 = \frac{\tilde{v}}{V} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{p^{\delta^* F}}, \quad (5.13b)$$

where \vec{v}_1 , and \tilde{v}_1 are respective rates per unit volume.

Eq. (5.12) is on the other hand transformed for the heterogeneous elementary reaction occurring in identical sites σ^* 's of total number G . $QC_0^{\delta^*}$, p^{δ^*} and $\Theta_{\sigma^*(\sigma^*)}$ involved in the expression are, now in accordance with Section 5.3, those of the assembly containing one δ^* in either one of σ^* . It follows that $G\Theta_{\sigma^*(\sigma^*)}=1$ or $\Theta_{\sigma^*(\sigma^*)} = 1/G$, i.e. that Eq. (5.12) assumes the form,

$$\vec{v}_1 = \frac{\vec{v}}{A} = \kappa \frac{kT}{h} G_1 \frac{q_{\sigma^*}^{\delta^*}}{p^{\delta^* I}} \Theta_{\sigma^*(0)}, \quad (5.14a)$$

$$\tilde{v}_1 = \frac{\tilde{v}}{A} = \kappa \frac{kT}{h} G_1 \frac{q_{\sigma^*}^{\delta^*}}{p^{\delta^* F}} \Theta_{\sigma^*(0)}, \quad (5.14b)$$

where A is the area of the surface and G_1 is the number of σ^* 's per unit area. The total rate may be obtained by simply summing up \vec{v}_1 , or \tilde{v}_1 , of Eq. (5.14a) or Eq. (5.14b) with respect to all kinds of sites.

6. Application-III. The characteristic number on the reaction

6.1. The order of reaction

The order m of a reaction has hitherto been taken the characteristic number of the reaction and the most important information about the mechanism.

Let the homogeneous fluid of our assembly contain members δ_l^L 's of the reactant, respectively, at concentrations $N^{\delta_l^L}$'s but none of the resultant, the former passing over into the reactant at a rate \vec{r}_0 per unit volume of the fluid. The number m is expressed as

$$m = \sum_l \frac{\partial \log \vec{r}_0}{\partial \log N^{\delta_l^L}}. \quad (6.1)$$

The individual term $\partial \log \vec{r}_0 / \partial \log N^{\delta_l^L}$ on the right-hand side of Eq. (6.1) gives what is called the order of reaction m_l^L with respect to δ_l^L , i.e.

$$m_l^L = \frac{\partial \log \vec{r}_0}{\partial \log N^{\delta_l^L}}. \quad (6.2)$$

¹⁴ cf. Section 5.3.

We consider on the basis of rate expressions advanced in Section 5.4, how the order of reaction indicates the mechanism, first with the homogeneous simple reaction,¹⁵ assuming throughout that κ remains constant with progress of the reaction.

We have in this case according to the definition,

$$\begin{aligned} \bar{r}_0 &\equiv \bar{v}_1, \\ \delta^L &\equiv \delta^I, \quad \delta^R \equiv \delta^F \end{aligned} \quad (6.3)$$

and

$$p^{\delta^L} \equiv p^{\delta^I}, \quad (6.4.L)$$

$$p^{\delta^R} \equiv p^{\delta^F}, \quad (6.4.R)$$

where \bar{v}_1 is the rate of the elementary reaction reckoned per unit volume of the homogeneous fluid. Expressing p^{δ^L} and p^{δ^R} according to Eqs. (2.11) and (5.2) in the forms,

$$p^{\delta^L} = \prod^l (p^{\delta_l^L})^{v_l^L}, \quad (6.5.L)$$

$$p^{\delta^R} = \prod^r (p^{\delta_r^R})^{v_r^R}, \quad (6.5.R)$$

we have by Eqs. (3.5), (5.13a), (6.3), (6.4.L) and (6.5.L)

$$\bar{r}_0 = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{\prod^l (Q^{\delta_l^L})^{v_l^L}} \prod^l (N^{\delta_l^L})^{v_l^L}, \quad (6.6)$$

i.e. that \bar{r}_0 is proportional to $\prod^l (N^{\delta_l^L})^{v_l^L}$ provided that components of variable concentration behave ideal so that Q^{δ} 's remain constant in the course of the reaction. The order is now given according to Eqs. (6.1), (6.2) and (6.6) as

$$m = \sum_l v_l^L \quad (6.7)$$

and

$$m_l^L = v_l^L. \quad (6.8)$$

The order of reaction m_l^L with respect to δ_l^L hence equals the number of the molecule δ_l^L reacting and m the total number of such molecules. Conversely, if observed value, of m_l^L , respectively, equals the stoichiometrical coefficient v_l^L of the chemical equation, the

mechanism may well be that of the simple reaction but not necessarily.

In the case when the simple reaction is heterogeneous the same is true with m and m_l^L since \bar{r}_0 or \bar{v}_1 , is, as in the previous case, proportional to $\prod^l (N^{\delta_l^L} / Q^{\delta_l^L})^{v_l^L}$ in the homogeneous fluid according to Eqs. (3.5), (5.14a), (6.3), (6.4.L) and (6.5.L), provided that $Q^{\delta_l^L}$'s and $q_{\sigma^*}^{\delta^*} \Theta_{\sigma^*(0)}$ in Eq. (5.14a) remain constant.

Passing now to the homogeneous reaction consisting of several elementary reactions, where every component of variable concentration behaves ideal, we first observe that \bar{r}_0 is proportional to \bar{v}_1 , of the rate-determining step, if not identical with, as in the case of simple reaction, that \bar{v}_1 , in turn depends solely on p^{δ^I} of the step because of the ideality according to Eq. (5.13a), that p^{δ^I} in turn is combined solely with $p^{\delta_l^L}$ 's¹⁶ because of the equilibrium relation Eq. (3.6) prevailing, according to Section 5.2, (ii), with all other elementary reactions than the rate-determining step, and that p^{δ^I} in turn depends only upon $N^{\delta_l^L}$ according to Eq. (3.5). The order m_l^L may hence be expressed according to Eq. (6.2) in the form,

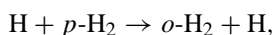
$$m_l^L = \frac{\partial \log \bar{r}_0}{\partial \log N^{\delta_l^L}} = \frac{\partial \log \bar{r}_0}{\partial \log p^{\delta^I}} \frac{\partial \log p^{\delta^I}}{\partial \log p^{\delta_l^L}} \frac{\partial \log p^{\delta_l^L}}{\partial \log N^{\delta_l^L}}.$$

Both the first and third differential coefficients of the third member of the equation being -1 according to Eqs. (3.5) and (5.13a), we have

$$m_l^L = \frac{\partial \log p^{\delta^I}}{\partial \log p^{\delta_l^L}}$$

which depends on the mechanism of the reaction.

In the case of the homogeneous *para-ortho*-conversion of hydrogen, if the rate-determining step is elementary reaction,



we have between $\delta^L \equiv p\text{-H}_2$ and $\delta^I \equiv \text{H} + p\text{-H}_2$ the equilibrium relation,

$$(p^{p\text{-H}_2})^{3/2} = p^{\text{H}} p^{p\text{-H}_2}$$

¹⁵ cf. Section 5.1.

¹⁶ The form of the function $p^{\delta^I} = p^{\delta^I}(p^{\delta_1^L}, p^{\delta_2^L}, \dots, p^{\delta_l^L})$ depends on the mechanism.

and hence

$$m = m_l^L = \frac{3}{2}.$$

The number m or m_l^L , if determined experimentally, gives thus a criterion for the mechanism.

The same is true with the heterogeneous reaction provided that component of variable concentration behaves ideal and $q_{\sigma^*}^{\delta^*} \Theta_{\sigma^*(0)}$ in Eq. (5.14a) remains sufficiently constant.

The above procedure of providing a criterion for the mechanism may be useful in the case of the homogeneous reaction, when we can often foresee the ideality on the ground of the small concentration of variable composition, but less in the case of the heterogeneous reaction when we can hardly be sure whether $q_{\sigma^*}^{\delta^*} \Theta_{\sigma^*(0)}$ is sufficiently constant before we learn anything about the mechanism.¹⁷

6.2. The stoichiometric number of the reaction

We first define the rate of the reaction in the forward direction as the number \vec{v} of reactants passing over into the resultant per unit time. The \vec{v} may be experimentally determined by distinguishing reactants originally present from those produced by the backward reaction, labelling the reactants or resultants, say, by means of isotopes. Since one act of the rate-determining step in the forward direction is necessary and sufficient for its reacting complex to pass from the state of the reactant into that of resultant,¹⁸ we have

$$\mu \vec{v} = \vec{v}, \quad (6.9a)$$

where μ is the number of forward acts of rate-determining step required to transfer one reactant completely to a resultant.

The backward rate \tilde{v} defined similarly bears a relation to \vec{v}

$$\mu \tilde{v} = \tilde{v}. \quad (6.9b)$$

Numerical values of \vec{v} or \tilde{v} hence depends, although the product $\mu \vec{v}$ or $\mu \tilde{v}$ is fixed, on the absolute value of the coefficient in the relevant chemical equation, where only the ratio among them needs to be

fixed. We refer here for the sake of concreteness μ , \vec{v} and \tilde{v} to the smallest possible intergral coefficients. We will call the characteristic number of the reaction μ thus fixed the stoichiometric number and proceed to express it in the form accessible to the experimental determination.

The observable resultant rate \vec{r} of decrease of reactant is given by

$$\vec{r} = \vec{v} - \tilde{v}. \quad (6.10)$$

We see, on the other hand, that by passing of one reactant over into the resultant the Zs of the assembly is multiplied by a factor $p^{\delta^R}/p^{\delta^L}$, inasmuch as the intermediate product of the steady reaction changes meanwhile hardly in concentration.¹⁹ The multiplication being, however, overall result of elementary reaction involved, it equals the multiplication due to the rate-determining step $p^{\delta^F}/p^{\delta^I}$, raised to μ th power, i.e.

$$\frac{p^{\delta^R}}{p^{\delta^L}} = \left(\frac{p^{\delta^F}}{p^{\delta^I}} \right)^\mu \quad (6.11)$$

since Zs remains unaffected because of the equilibrium relation Eq. (3.6) by any other elementary reaction than the rate-determining step according to Section 5.2, (ii).

The argument $p^{\delta^F}/p^{\delta^I}$ on the right-hand side of Eq. (6.11) equals \vec{v}/\tilde{v} as it follows immediately from Eqs. (5.6a) and (5.6b), i.e.

$$\frac{\vec{v}}{\tilde{v}} = \frac{p^{\delta^F}}{p^{\delta^I}}. \quad (6.12)$$

Eliminating now $p^{\delta^F}/p^{\delta^I}$, \vec{v} , \tilde{v} and \tilde{v} from Eqs. (6.9a)–(6.12), we have

$$\vec{r} = \vec{v} \left\{ 1 - \left(\frac{p^{\delta^L}}{p^{\delta^R}} \right)^{1/\mu} \right\}, \quad (6.13)$$

or differentiating with respect to

$$x = \frac{p^{\delta^L}}{p^{\delta^R}}, \quad (6.14)$$

$$\frac{\partial \vec{r}}{\partial x} = \frac{\partial \vec{v}}{\partial x} (1 - x^{1/\mu}) - \frac{1}{\mu} \vec{v} x^{1/\mu-1}$$

¹⁷ cf. Section 8.1.

¹⁸ cf. Section 5.2, (i).

¹⁹ cf. Section 5.2.

or at equilibrium of the reaction when $x = 1$,

$$\frac{1}{\mu} = -\frac{1}{\vec{v}_{\text{Eq}}} \left(\frac{\partial \vec{r}}{\partial x} \right)_{\text{Eq}} \quad (6.15)$$

or according to Eqs. (3.25) and (6.14)

$$\frac{1}{\mu} = \frac{RT}{\vec{v}_{\text{Eq}}} \left(\frac{\partial \vec{r}}{\partial (\mu^{\delta\text{L}} - \mu^{\delta\text{R}})} \right)_{\text{Eq}}, \quad (6.16)$$

where the suffix ‘Eq’ signifies the values at equilibrium.

The number μ is expressed in a slightly different form by differentiating \vec{r} with respect to $p^{\delta\text{L}}$: the result is, according to Eqs. (6.5.L), (6.13) and (6.14),

$$\frac{\partial \vec{r}}{\partial p^{\delta\text{L}}} = \frac{\partial \vec{v}}{\partial p^{\delta\text{L}}} (1 - x^{1/\mu}) - \vec{v}_l^{\text{L}} \frac{x^{1/\mu}}{\mu p^{\delta\text{L}}}$$

or at equilibrium

$$\frac{v_l^{\text{L}}}{\mu} = -\frac{1}{\vec{v}_{\text{Eq}}} \left(\frac{\partial \vec{r}}{\partial \log p^{\delta\text{L}}} \right)_{\text{Eq}} \quad (6.17)$$

or by Eq. (3.25)

$$\frac{v_l^{\text{L}}}{\mu} = \frac{RT}{\vec{v}_{\text{Eq}}} \left(\frac{\partial \vec{r}}{\partial \mu^{\delta\text{L}}} \right)_{\text{Eq}}. \quad (6.18)$$

Eq. (6.16) or Eq. (6.18) allows us to determine μ experimentally provided \vec{v}_{Eq} is observed for instance by a proper use of isotopes.

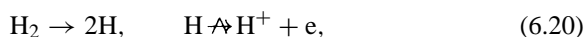
6.3. The stoichiometric number of the hydrogen electrode process

The fitting of an alternative mechanism to the observed value of μ is exemplified later with the hydrogen electrode process.

If the hydrogen electrode reaction written down in the form,



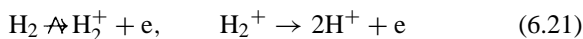
has the mechanism,



i.e. if H_2 splits first into adsorbed hydrogen atoms and then each atom dissociates further into a hydrogen ion H^+ and a metal electron e of the electrode and the latter step is the rate-determining, μ is 2, since then

the step should take place twice as frequently as the total reaction.

If on the other hand, the mechanism is such that,



or that H_2 splits first into the hydrogen molecule ion H_2^+ and a metal electron determining the rate, and H_2^+ then further into 2H^+ and e , μ must be 1.

The experimental determination of μ in the case of the hydrogen electrode process on platinum has been carried out by Horiuti and Ikusima [12]. The resultant current \vec{v}_{Eq} in Eq. (6.16) was measured by the electrode current, while \vec{v}_{Eq} by the rate of the exchange reaction between the hydrogen gas and the solution around the electrode [13,14] and $p^{\delta\text{L}}/p^{\delta\text{R}}$ by the relation,²⁰

$$-RT \log \frac{p^{\delta\text{L}}}{p^{\delta\text{R}}} = 2F\eta, \quad (6.22)$$

where F signifies Faraday and η the overvoltage of the electrode.²¹ We obtain from Eqs. (6.14), (6.15) and (6.22) noting that $p^{\delta\text{L}} = p^{\delta\text{R}}$ at equilibrium and hence $\eta = 0$, an expression;

$$\frac{1}{\mu} = \frac{RT}{2F\vec{i}_{\eta=0}} \left(\frac{\partial \vec{i}}{\partial \eta} \right)_{\eta=0}, \quad (6.23)$$

where $\vec{i}_{\eta=0}$ and \vec{i} are currents corresponding, respectively, to rates $\vec{v}_{E\delta}$ and \vec{r} .

²⁰ Eq. (6.22) is derived as follows. For the reversible hydrogen electrode we have the equilibrium relation according to Eq. (3.6), i.e.

$$p^{\text{H}_2} = (p^{\text{H}^+})^2 (p_0^{\text{e}})^2,$$

where p_0^{e} is the p^{δ} of the metal electron there. But since the reversible work of transferring $-F$ electricity from the reversible electrode into the electrode in question is $-F\eta$ by definition, we have

$$-RT \log \frac{p^{\text{e}}}{p_0^{\text{e}}} = -F\eta,$$

where p^{e} is that of the metal electron in the electrode. But since according to Eq. (6.19), $p^{\delta\text{L}} = p^{\text{H}_2}$ and $p^{\delta\text{R}} = (p^{\text{H}^+})^2 (p^{\text{e}})^2$, we have $p^{\delta\text{L}}/p^{\delta\text{R}} = (p_0^{\text{e}}/p^{\text{e}})^2$ and hence Eq. (6.22).

²¹ The overvoltage is defined as the electrode potential referred to any reversible hydrogen electrode in the same solution of the same hydrogen concentration as that in the direct neighbourhood of the electrode in question.

Horiuti and Ikusima [12] thus found that $\mu = 1$ for the hydrogen electrode process on platinum. The mechanism of Eq. (6.21) among the two alternatives advanced thus only fits the observed value of μ .

7. Application-IV. Homogeneous reaction

7.1. The rate of the homogeneous elementary reaction

We define k^x of the homogeneous elementary reaction in accordance with Eqs. (3.5), (5.7.I) and (5.13a) as

$$k^x = \frac{\bar{v}}{\prod^i (N_i^{\delta_i})^{v_i^I}} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{\prod^i (Q_i^{\delta_i})^{v_i^I}}, \quad (7.1)$$

where suffix x signifies $\sum_i v_i^I$ or the total number of molecules of the initial complex. The k^x is the “rate constant” as called usually but not necessarily a constant inasmuch as Q^{δ} 's in Eq. (7.1) may vary if δ 's are not ideal.

Denoting the quantities at infinite dilution of variable components by suffix 0, we have

$$k^x = \frac{\kappa}{\kappa_0} k_0^x \frac{\prod^i (f_i^{\delta_i})^{v_i^I}}{f^{\delta^*}}, \quad (7.2)$$

where

$$k_0^x = \kappa_0 \frac{kT}{h} \frac{Q_0^{\delta^*}}{\prod^i (Q_0^{\delta_i})^{v_i^I}}, \quad (7.3)$$

$$f^{\delta} = \frac{Q_0^{\delta}}{Q^{\delta}}. \quad (7.4)$$

The f^{δ} may be identified with activity coefficient inasmuch as it becomes unity at the infinite dilution and bears the relation to μ^{δ} according to Eqs. (3.81), (3.82) and (7.4)

$$\mu^{\delta} = \mu_{1,0}^{\delta} + RT \log f^{\delta} N^{\delta}, \quad (7.5)$$

where

$$\mu_{1,0}^{\delta} = -RT \log Q_0^{\delta}. \quad (7.6)$$

The relation of the form of Eq. (7.5) was advanced by Brønsted [15,16] and Wynne-Jones and Eyring [17] by analogy to thermodynamics regarding the activated

complex as thermodynamical chemical species without defining f^{δ} on the statistical mechanical basis.

In the case of a gas k_0^x is independent of the pressure, Q_0^{δ} 's being equal to that in vacuum. $Q_0^{\delta^*}$ is hence calculable with reference to a single reaction complex in vacuum.

7.2. The rate constant due to Eyring, Evans and Polanyi

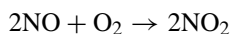
Eq. (7.1) or Eq. (7.3) is identical in the form with those obtained by Eyring [18], Evans and Polanyi [11] but not quite in its implication. The latter authors derive the identical form of Eq. (7.3) by defining the activated complex $\delta_E^*(g)$ arbitrarily with reference to the saddle point on the potential energy surface of an isolated $\bar{\delta}$ and by assuming the chemical equilibrium between the initial and the activated complex or by expressing the concentration $N^{\delta_E^*(g)}$ of the latter according to the equilibrium relation Eq. (4.9) as

$$N^{\delta_E^*(g)} = \frac{Q^{\delta_E^*(g)}}{\prod^i (Q_i^{\delta_i})^{v_i^I}} \prod^i (N_i^{\delta_i})^{v_i^I}. \quad (7.7)$$

Multiplying the latter by the “universal frequency” kT/h , the frequency of transition through the saddle point in the forward direction for $\delta_E^*(g)$ and by the chance κ “that having once crossed the barrier, the activated complex does not return,” [19] they arrive at the rate expression and hence at the identical form of Eq. (7.1). Extending now the latter form by analogy, they go back to that of Eq. (7.2) for the elementary reaction in liquid, Q^{δ^*} there being, according to them, that of quasi-gas molecule moving in the mean potential field of the environment.

It is implied in the theory of Eyring [20], Evans and Polanyi [11] that the saddle point is at least approximately narrowest pass on the path from the initial to the final state. This may be practically true in many cases but associated with difficulty in some cases.

Eyring assumes, for example, in accounting for the negative temperature coefficient of the elementary reaction,



that the activated complex consisting of the three molecules 2NO and O₂ has the same minimum potential energy as the initial complex, which corresponds

to the lowest possible saddle point [20]. As pointed out by Rice [21] however the temperature coefficient cannot be zero or negative if such saddle point is even approximately narrowest to pass through. This difficulty is of course not associated with the present method where the critical complex is originally defined with reference to the narrowest configuration itself.

Another difficulty with their method is due to the assumption of the equilibrium relation between the initial and the activated complex. We consider first the state of equilibrium between the initial and the final complex and then that of the irreversible state brought about from the former by removing the final complex. If the transmission coefficient is unity or the reacting complex which transits the state of the activated complex forward, originate all in the initial complex, the rate of the transition remains of course unaffected by removing of the final complex. The equilibrium relation is then applicable in this sense which is assumed by Wynne-Jones and Eyring [17] for general validity.

The assumption is not, however, legitimate even in this sense when the transmission coefficient is appreciably less than unity, or, when only a small fraction of the reaction complexes once traversed the activated state completes the elementary reaction.²² Admitting with Eyring, Evans and Polanyi that the activated state is the narrowest pass throughout the course from the initial to the final state, we may conclude that at equilibrium the activated complex transiting in either direction will equally likely reach the initial as well as the final state, and any one there is equally likely having come from the either state. By removing now the final complex in this case, the activated complex, which originating in the final complex transits the activated state forward, falls off, the total number of activated complexes transiting forward being thus almost halved. The equilibrium relation is thus inapplicable here even in the above sense.

This latter difficulty is, however, only formal, since the final rate expression Eq. (7.1) or Eq. (7.3), of the identical form is derived according to the present method without resorting to the equilibrium relation.

It seems to the present author that Fowler [22], Guggenheim and Weiss [23] criticises the method of

Eyring [18], Evans and Polanyi [11] because of the equilibrium relation with the conception of the latter case or that of the diffusion-type as called by the present author [8,9] whereas Eyring, Evans and Polanyi [24] defend with the conception of the former case or that of the effusion type. They both are justified so far as the respective extreme case is concerned.

Rabinowitch [25], Christiansen [26,27] and Norrish [28] follow a different line of developing the theory of the elementary reaction from that of Eyring [18], Evans and Polanyi [11] with special reference to the diffusion type. The procedure of the former group of authors seems, however, to be looked upon by Eyring as an alternative manner of describing the unique reality,²³ rather than as dealing, as actually they are, with the other extremity of the reality.

Experimental materials hitherto found unfortunately fit the picture of the effusion type, or equally well the both. It is desirable to find examples which, fitting exclusively that of the diffusion type, lead us inevitably to the correct synthesis of these antithesis.

7.3. The thermodynamical form of the homogeneous rate

In this section, the rate and the rate constant will be expressed in thermodynamical terminology: it is however neither claimed nor needs to be claimed thereby that the critical complex behaves like a thermodynamical chemical species or that recognized directly by thermodynamical (stoichiometrical) procedure; every quantity and relation here dealt with are purely of the statistical mechanical formulation being clad in thermodynamical terms.

Eq. (5.6a) for the rate of the elementary reaction is expressed by substituting p^δ 's formally from Eq. (3.25) with due regard to Eqs. (3.72.μ), (3.73.μ) and (5.7.1) as follows:

$$\bar{v} = \kappa \frac{kT}{h} e^{-\Delta|^\ast F_V/RT} = \kappa e^{-\Delta|^\ast Z_P/RT}, \quad (7.8)$$

where

$$\begin{aligned} \Delta|^\ast F_V &= \bar{F}_V^{\delta^\ast} - \sum_i \nu_i^I \bar{F}_i^{\delta_i^I} \\ &= \Delta|^\ast Z_P = \bar{Z}_P^{\delta^\ast} - \sum_i \nu_i^I \bar{Z}_i^{\delta_i^I}. \end{aligned} \quad (7.9)$$

²² We consider here only elementary reactions which proceed adiabatically, cf. Section 5.3.

²³ cf. Eyring's comment on the work of Christiansen [27].

Denoting the critical increment of any extensive property by prefix $\Delta|^*$ and the associated condition of constant volume or of constant pressure, respectively, by suffix V or P as above we have from Eqs. (3.72.μ), (3.73.μ) and (3.74.μ)

$$\begin{aligned}\Delta|^*F_V &= \Delta|^*Z_P = \Delta|^*U_V - T\Delta|^*S_V \\ &= \Delta|^*X_P - T\Delta|^*S_P\end{aligned}\quad (7.10)$$

and hence Eq. (7.8) in the form,

$$\begin{aligned}\bar{v} &= \kappa \frac{kT}{h} e^{\Delta|^*S_V/R} e^{-\Delta|^*U_V/RT} \\ &= \kappa \frac{kT}{h} e^{\Delta|^*S_P/R} e^{-\Delta|^*X_P/RT}.\end{aligned}\quad (7.11)$$

Eq. (7.1) for k^x is expressed according to Eqs. (3.82) and (3.93.μ) in the form,

$$k^x = \kappa \frac{kT}{h} e^{-\Delta|^*F_{V,1}/RT} = \kappa \frac{kT}{h} e^{-\Delta|^*Z_{P,1}/RT}, \quad (7.12)$$

where

$$\begin{aligned}\Delta|^*F_{V,1} &= \bar{F}_{V,1}^{\delta^*} - \sum_i v_i^I \bar{F}_{V,1}^{\delta_i^I} = \Delta|^*Z_{P,1} \\ &= \bar{Z}_{P,1}^{\delta^*} - \sum_i v_i^I \bar{Z}_{P,1}^{\delta_i^I} = \mu_1^{\delta^*} - \sum_i v_i^I \mu_1^{\delta_i^I}.\end{aligned}\quad (7.13)$$

Defining increments $\Delta|^*U_{V,1}$, $\Delta|^*X_{P,1}$, $\Delta|^*S_{V,1}$ and $\Delta|^*S_{P,1}$ of the “standard state” similarly as $\Delta|^*F_{V,1}$ or $\Delta|^*Z_{P,1}$, k^x is further expressed according to Eq. (3.97) in the form,

$$\begin{aligned}k^x &= \kappa \frac{kT}{h} e^{-(\Delta|^*U_{V,1} - T\Delta|^*S_{V,1})/RT} \\ &= \kappa \frac{kT}{h} e^{-(\Delta|^*X_{P,1} - T\Delta|^*S_{P,1})/RT},\end{aligned}\quad (7.14)$$

where

$$\begin{aligned}\Delta|^*F_{V,1} &= \Delta|^*U_{V,1} - T\Delta|^*S_{V,1} = \Delta|^*Z_{P,1} \\ &= \Delta|^*X_{P,1} - T\Delta|^*S_{P,1}.\end{aligned}\quad (7.15)$$

Critical increments and k^x are constant at constant temperature and pressure provided that components of variable concentration are ideal and κ , α , and β remain, respectively, constant.

Interrelations among critical increments are readily derived from the relations among partial molar quantities developed in Section 3.9 and 3.10 as follows:

$$\Delta|^*F_V = \Delta|^*Z_P = \Delta|^*F_P + P\Delta|^*V_P, \quad (7.16.F)$$

$$\Delta|^*S_P = \Delta|^*S_V + \frac{\alpha}{\beta} \Delta|^*V_P, \quad (7.16.S)$$

$$\begin{aligned}\Delta|^*X_P &= \Delta|^*U_V + T\frac{\alpha}{\beta} \Delta|^*V_P \\ &= \Delta|^*U_P + P\Delta|^*V_P,\end{aligned}\quad (7.16.X)$$

$$\left(\frac{\partial \Delta|^*F_V}{\partial T}\right)_V = -\Delta|^*S_V, \quad (7.16.FS)$$

$$\left(\frac{\partial \Delta|^*Z_P}{\partial T}\right)_P = -\Delta|^*S_P, \quad (7.16.ZS)$$

$$\left(\frac{\partial \Delta|^*F_V}{\partial P}\right)_T = \left(\frac{\partial \Delta|^*Z_P}{\partial P}\right)_T = \Delta|^*V_P, \quad (7.16.FV)$$

$$\Delta|^*F_{V,1} = \Delta|^*Z_{P,1} = \Delta|^*F_{P,1} + P\Delta|^*V_P, \quad (7.17.F)$$

$$\Delta|^*S_{P,1} = \Delta|^*S_{V,1} + \frac{\alpha}{\beta} \Delta|^*V_P, \quad (7.17.S)$$

$$\begin{aligned}\Delta|^*X_{P,1} &= \Delta|^*U_{V,1} + T\frac{\alpha}{\beta} \Delta|^*V_P \\ &= \Delta|^*U_{P,1} + P\Delta|^*V_P,\end{aligned}\quad (7.17.X)$$

$$\left(\frac{\partial \Delta|^*F_{V,1}}{\partial T}\right)_V = -\Delta|^*S_{V,1}, \quad (7.17.FS)$$

$$\left(\frac{\partial \Delta|^*Z_{P,1}}{\partial T}\right)_P = -\Delta|^*S_{P,1} + v^*RT\alpha, \quad (7.17.ZS)$$

$$\begin{aligned}\left(\frac{\partial \Delta|^*F_{V,1}}{\partial P}\right)_T &= \left(\frac{\partial \Delta|^*Z_{P,1}}{\partial P}\right)_T \\ &= \Delta|^*V_P - v^*RT\beta,\end{aligned}\quad (7.17.FV)$$

$$\left(\frac{\partial \Delta|^*X_{P,1}}{\partial P}\right)_T = \Delta|^*V_P - T\left(\frac{\partial \Delta|^*V_P}{\partial T}\right)_P, \quad (7.18)$$

$$\begin{aligned}\Delta|^*F_{V,1} &= \Delta|^*F_V - RT\overline{\log N^*} = \Delta|^*Z_{P,1} \\ &= \Delta|^*Z_P - RT\overline{\log N^*},\end{aligned}\quad (7.19.F)$$

$$\Delta|^*S_{V,1} = \Delta|^*S_V + R\overline{\log N^*}, \quad (7.19.S_V)$$

$$\Delta|^*S_{P,1} = \Delta|^*S_P + R\overline{\log N^*}, \quad (7.19.S_P)$$

$$\Delta|^*U_{V,1} = \Delta|^*U_V, \quad (7.19.U)$$

$$\Delta|^*X_{P,1} = \Delta|^*X_P, \quad (7.19.X)$$

where

$$\overline{\log N}^{\delta^*} = \log N^{\delta^*} - \sum_i \log v_i^I \log N^{\delta_i^I} \quad (7.20.N)$$

and

$$v^* = 1 - \sum_i v_i^I. \quad (7.20.v)$$

In the special case of a gas when

$$\Delta|^*V_P = v^* \frac{RT}{P}, \quad (7.21.V)$$

$$\alpha = \frac{1}{T} \quad (7.21.\alpha)$$

and

$$\beta = \frac{1}{P}, \quad (7.21.\beta)$$

Eqs. (7.16), (7.17) and (7.18) assume, respectively, the forms,

$$\Delta|^*F_V = \Delta|^*Z_P = \Delta|^*F_P + v^*RT, \quad (7.22.F)$$

$$\Delta|^*S_P = \Delta|^*S_V + v^*R, \quad (7.22.S)$$

$$\Delta|^*X_P = \Delta|^*U_V + v^*RT = \Delta|^*U_P + v^*RT, \quad (7.22.X)$$

$$\Delta|^*U_V = \Delta|^*U_P = \Delta|^*U, \quad (7.22.U)$$

$$\left(\frac{\partial \Delta|^*F_V}{\partial T}\right)_V = -\Delta|^*S_V, \quad (7.22.FS)$$

$$\left(\frac{\partial \Delta|^*Z_P}{\partial T}\right)_P = -\Delta|^*S_P, \quad (7.22.ZS)$$

$$\left(\frac{\partial \Delta|^*F_V}{\partial P}\right)_T = \left(\frac{\partial \Delta|^*Z_P}{\partial P}\right)_T = v^* \frac{RT}{P}, \quad (7.22.FV)$$

$$\Delta|^*F_{V,1} = \Delta|^*Z_{P,1} = \Delta|^*F_{P,1} + v^*RT, \quad (7.23.F)$$

$$\Delta|^*S_{V,1} = \Delta|^*Z_{P,1} + v^*R, \quad (7.23.S)$$

$$\Delta|^*X_{P,1} = \Delta|^*U_{V,1} + v^*RT = \Delta|^*U_{P,1} + v^*RT, \quad (7.23.X)$$

$$\Delta|^*U_{V,1} = \Delta|^*U_{P,1}, \quad (7.23.U)$$

$$\left(\frac{\partial \Delta|^*F_{V,1}}{\partial T}\right)_V = -\Delta|^*S_{V,1}, \quad (7.23.FS)$$

$$\left(\frac{\partial \Delta|^*Z_{P,1}}{\partial T}\right)_P = -\Delta|^*S_{P,1} + v^*R, \quad (7.23.VS)$$

$$\left(\frac{\partial \Delta|^*F_{V,1}}{\partial P}\right)_T = \left(\frac{\partial \Delta|^*Z_{P,1}}{\partial P}\right)_T = 0, \quad (7.23.FV)$$

$$\left(\frac{\partial \Delta|^*X_{P,1}}{\partial P}\right)_T = 0, \quad (7.23.XV)$$

whereas Eq. (7.19) remains intact.

7.4. The temperature variation of the rate and the rate constant

Our treatment for the variation of the rate with temperature will be restricted to the elementary reaction of the effusion type²⁴ for which κ is constantly unity. The temperature variation of the rate \vec{v} is readily expressed according to Eq. (7.8) in the form,

$$RT^2 \left(\frac{\partial \log \vec{v}}{\partial T}\right)_P = RT + \Delta|^*Z_P - T \left(\frac{\partial \Delta|^*Z_P}{\partial T}\right)_P \quad (7.24.P)$$

and

$$RT^2 \left(\frac{\partial \log \vec{v}}{\partial T}\right)_V = RT + \Delta|^*F_V - T \left(\frac{\partial \Delta|^*F_V}{\partial T}\right)_V \quad (7.24.V)$$

and hence according to Eqs. (7.10) and (7.16)

$$RT^2 \left(\frac{\partial \log \vec{v}}{\partial T}\right)_P = RT + \Delta|^*X_P, \quad (7.25.P)$$

$$RT^2 \left(\frac{\partial \log \vec{v}}{\partial T}\right)_V = RT + \Delta|^*U_V. \quad (7.25.V)$$

The temperature variation of the rate constant of the elementary reaction is expressed in the form of the Arrhenius activation energy by differentiation of Eq. (7.12), i.e.

$$RT^2 \left(\frac{\partial \log k^x}{\partial T}\right)_P = RT + \Delta|^*Z_{P,1} - T \left(\frac{\partial \Delta|^*Z_{P,1}}{\partial T}\right)_P, \quad (7.26.P)$$

²⁴ See Section 7.2 cf. [8,9].

$$RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_V = RT + \Delta|^*F_{V,1} - T \left(\frac{\partial \Delta|^*F_{V,1}}{\partial T} \right)_V, \quad (7.26.V)$$

and according to Eqs. (7.15) and (7.17)

$$RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_P = RT + \Delta|^*X_P - \nu^*RT^2\alpha, \quad (7.27.P)$$

$$RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_V = RT + \Delta|^*U_V. \quad (7.27.V)$$

The difference between the above two forms of the temperature variation is expressed according to Eq. (7.16.X) as

$$RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_P - RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_V = T \frac{\alpha}{\beta} \Delta|^*V_P - \nu^*RT^2\alpha. \quad (7.28)$$

Assuming that $T = 300$ K, $\Delta|^*V_P = 100$ ml, $\alpha = 10^{-3}$ per degree, $\beta = 10^{-4}$ atm $^{-1}$ and $\nu^* = -1$ which corresponds to the ordinary case of the bimolecular elementary reaction in liquid, we find 7 kcal for the difference which is by no means negligible.

The expression for the difference is derived by Evans and Polanyi [11] raising the importance of the ‘‘Arrhenius activation energy at constant volume’’ $RT^2(\partial \log k^x/\partial T)_V$ for elucidation of the reaction mechanism in liquid who, however, leave out the second term $\nu^*RT^2\alpha$ in the above equation.

The latter term, although minor in the above example of the liquid assembly, becomes so large in gas that it just cancels the first according to Eq. (7.21). Both the ‘‘activation energies’’ are now identical with each other being given as

$$RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_P = RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_V = RT + \Delta|^*U,$$

where

$$\Delta|^*U = \Delta|^*U_P = \Delta|^*U_V.$$

7.5. Pressure variation of the rate

Our treatment of the pressure variation is restricted as noted in the foregoing section to the case of effu-

sion type. We have readily according to Eqs. (7.8) and (7.16.FV)

$$\left(\frac{\partial \log \bar{v}}{\partial P} \right)_T = \frac{\Delta|^*V_P}{RT}. \quad (7.29)$$

Similar expression for k^x is obtained from Eqs. (7.12) and (7.17.FV) as

$$\left(\frac{\partial \log k^x}{\partial P} \right)_T = -\frac{\Delta|^*V_P}{RT} + \beta\nu^*. \quad (7.30)$$

Differentiating Eq. (7.27.P) with respect to P with regard to Eq. (7.18), or Eq. (7.30) with respect to T , we have

$$\frac{\partial^2 \log k^x}{\partial T \partial P} = \frac{\Delta|^*V_P}{RT^2} - \frac{1}{RT} \left(\frac{\partial \Delta|^*V_P}{\partial T} \right)_P + \nu^* \left(\frac{\partial \beta}{\partial T} \right)_P$$

or

$$\left(\frac{\partial E_P}{\partial P} \right)_T = \Delta|^*V_P \left\{ 1 - T \left(\frac{\partial \log \Delta|^*V_P}{\partial T} \right)_P \right\} - \nu^*RT^2 \left(\frac{\partial \alpha}{\partial P} \right)_T, \quad (7.31)$$

where

$$E_P = RT^2 \left(\frac{\partial \log k^x}{\partial T} \right)_P$$

and

$$\left(\frac{\partial \alpha}{\partial P} \right)_T = \frac{\partial^2 \log V}{\partial P \partial T} = - \left(\frac{\partial \beta}{\partial T} \right)_P.$$

Evans and Polanyi [29] and Guggenheim [30] derived, respectively, the similar expression for $(\partial E_P/\partial P)_T$, the former authors, however, leaving out the term $\nu^*RT^2(\partial \alpha/\partial P)_T$, whereas the latter including a term valid in the special case of the bimolecular association when $\nu^* = -1$.

7.6. Comment on the controversies on the thermodynamical treatment of the rate

As detailed in the foregoing section due distinction must be made, for exact thermodynamical treatment of the rate, between the partial molar quantities and the total quantities on the one hand, and, between the critical increments at constant pressure and those at constant volume on the other hand except in the case of the gas. Such a distinction is of course not merely

the matter of the thermodynamical treatment of the rate, but might be directed back to the pure thermodynamical treatment of the equilibrium.

Less precaution seems to have hitherto been paid on this respect, as might naturally be expected from the history of the theory of the rate developed in analogy to the thermodynamical theory of equilibrium in a gas. The situation seems, however, to have resulted in unfortunate confusions and controversies, which are going to be analysed and commented upon hereafter in the light of the present thermodynamical theory of the rate.

Moelwyn-Hughes [31] puts forward the following expression for the dependence of the Arrhenius activation energy E_A on hydrostatical pressure P ,

$$E_A = \Delta|^\ast E + P\Delta|^\ast V \times \left\{ 1 - T \left(\frac{\partial \log \Delta|^\ast V}{\partial T} \right)_P - T \left(\frac{\partial \log P}{\partial T} \right)_V \right\}, \quad (7.32)$$

where $\Delta|^\ast E$ or $\Delta|^\ast V$ is, as he states, the increase in internal energy or volume associated with the change from ordinary to activated molecules.

Evans and Polanyi [29] advance another expression,

$$E_A = E_0 + P\Delta|^\ast V \left\{ 1 - T \left(\frac{\partial \log \Delta|^\ast V}{\partial T} \right)_P \right\} \quad (7.33)$$

for the relation, where E_0 is E_A at $P = 0$. The latter expression may be derived along the line of procedure of Evans and Polanyi by neglecting $RT^2 v^\ast (\partial \alpha / \partial P)_T$ identifying E_A to E_P in Eq. (7.31) and integrating the latter with respect P , regarding

$$\Delta|^\ast V \left\{ 1 - T \left(\frac{\partial \log \Delta|^\ast V}{\partial T} \right)_P \right\}$$

constant. Evans and Polanyi [32] claim Moelwyn-Hughes's Eq. (7.32) contradicts thermodynamics, because the latter is inconsistent, as they prove, with their Eq. (7.33).

Moelwyn-Hughes starts from the assumption

$$k_0^x = \text{const.} \times e^{-\Delta|^\ast \varphi / RT} \quad (7.34)$$

and

$$\Delta|^\ast \varphi = \Delta|^\ast E + P\Delta|^\ast V - T\Delta|^\ast S, \quad (7.35)$$

where $\Delta|^\ast \varphi$ is, as he states, the critical increment of the (Helmholtz's) free energy. By differentiation of Eq. (7.34) he arrives at Eq. (7.32).

In order to follow his line of reasoning exactly the critical increments involved in the assumption, $\Delta|^\ast \varphi$, $\Delta|^\ast E$, $\Delta|^\ast S$ and $\Delta|^\ast V$ have to be distinguished with respect to their associated conditions. For being the increment of the Helmholtz's free energy, $\Delta|^\ast \varphi$ must be any one of $\Delta|^\ast F_{V,1}$, $\Delta|^\ast F_{P,1}$, $\Delta|^\ast F_V$, and $\Delta|^\ast F_P$. It must be however either $\Delta|^\ast F_{V,1}$ or $\Delta|^\ast F_{P,1}$ rather than $\Delta|^\ast F_V$ or $\Delta|^\ast F_P$ since otherwise, k_0^x depends necessarily on the concentrations of the initial complex. The $\Delta|^\ast F_{V,1}$ is expressed according to Eqs. (7.15) and (7.17.X) as

$$\Delta|^\ast F_{V,1} = \Delta|^\ast U_{P,1} + P\Delta|^\ast V_P - T\Delta|^\ast S_{P,1}, \quad (7.36.V)$$

whereas $\Delta|^\ast F_{P,1}$ according to Eq. (7.17.F) as

$$\Delta|^\ast F_{P,1} = \Delta|^\ast U_{P,1} - T\Delta|^\ast S_{P,1}. \quad (7.36.P)$$

We see that for $\Delta|^\ast V_P$ to persist in the expression of $\Delta|^\ast \varphi$, the latter must be expressed by Eq. (7.36.V) which fixes the exact meaning of notations in Eq. (7.35). Moelwyn-Hughes' Eq. (7.32) appears now in the form,

$$E_A = \Delta|^\ast U_{P,1} + P\Delta|^\ast V_P \times \left\{ 1 - T \left(\frac{\partial \log \Delta|^\ast V_P}{\partial T} \right)_P - T \left(\frac{\partial \log P}{\partial P} \right)_V \right\}. \quad (7.37)$$

By Eqs. (7.15), (7.17), (7.34) and (7.36) we have however, either

$$RT^2 \left(\frac{\partial \log k_0^x}{\partial T} \right)_P = \Delta|^\ast X_P - v^\ast RT^2 \alpha \quad (7.38.P)$$

or

$$RT^2 \left(\frac{\partial \log k_0^x}{\partial T} \right)_V = \Delta|^\ast U_V. \quad (7.38.V)$$

Equating the former to the Arrhenius activation energy E_A , which is according to Evans and Polanyi [32] always to be referred to constant pressure, and transforming $\Delta|^\ast X_P$ by Eq. (7.17.X), we have

$$E_A = E_P = \Delta|^\ast U_{P,1} + P\Delta|^\ast V_P - v^\ast RT^2 \alpha. \quad (7.39)$$

We see that differential coefficients $T(\partial \log \Delta|^{*}V_P/\partial T)_P$ as well as $T(\partial \log P/\partial T)_V$ in Eq. (7.37) are here missing, the term $v^{*}RT^2\alpha$ appearing instead.

Evans and Polanyi, criticizing Moelwyn-Hughes' procedure of deriving his Eq. (7.32), state that the appearance of the third term $T(\partial \log P/\partial T)_V$ in the parenthesis is due to a mistake of differentiation and by performing the differentiation correctly an expression without the term $T(\partial \log P/\partial T)_V$ in coincidence with their Eq. (7.33) is obtained. But we see above that by carrying out the differentiation more correctly even the term $T(\partial \log \Delta|^{*}V_P/\partial T)_P$ disappears, which affords a strong feature of resemblance of Eq. (7.32) with Eq. (7.33). The erroneous term $T(\partial \log \Delta|^{*}V_P/\partial T)_P$ creeps into the final expression, if the differentiation of $-(\Delta|^{*}U_{P,1} - T\Delta|^{*}S_{P,1})/RT$ with respect to T is incorrectly taken to be $\Delta|^{*}U_{P,1}/RT^2$ by analogy to the differentiation of $-(U - TS)/RT$ at constant volume, which gives exactly U/RT^2 according to Eqs. (3.21) and (3.23) or by analogy to the differentiation of $-(\Delta|^{*}U_{V,1} - T\Delta|^{*}S_{V,1})/RT$ at constant volume resulting exactly in $-\Delta|^{*}U_{V,1}/RT$ according to Eqs. (7.15) and (7.17FS).

It may be seen that the neglect of the distinction of the partial molar quantity from the total quantity and of the associated condition of the critical increment is quite misleading.

Guggenheim [30] developed the thermodynamical theory of the rate correctly, arriving at the identical forms of Eqs. (7.38.P) and (7.39) although the distinction between the constant pressure and the constant volume is not explicitly noted or rather all partial molar quantities are referred to constant pressure.

He starts thereby from the definition of the ideal dilute solution with the independent variables of temperature, pressure and mol fraction, giving quite different formulations for the thermodynamics in gas from that in liquid, whereas here the ideal solution is defined with the homogeneous fluid in accordance with Guggenheim's particular form in liquid, the other in gas being automatically derived as its special case. We note that the term $v^{*}RT^2\alpha$, in Eqs. (7.17.ZS), (7.27.P) and (7.28), taken into account with its particular value by Guggenheim, takes care, as shown in Section 7.3 and 7.4, with proper precaution on the condition of partial molar quantities, to include the thermodynam-

ics of the elementary reaction in gas as the special case.

On commenting on the papers of Moelwyn-Hughes and of Evans and Polanyi on the basis of his theory, Guggenheim [30] objects Evans and Polanyi's view that k_0^x should be differentiated at constant pressure on the ground that measured values of E_A at ordinary pressures as well as at hydrostatical pressure are all referred to constant pressure [32], stating that "the correct reason of keeping the pressure constant, is that temperature, pressure and mol fractions are the independent variables in the simple formula by which ideal systems have been defined and therefore also in all formula derived therefrom" [30]. We see no reason why we should be faithful to this set of variables throughout: with proper transformations and with proper specifications of associated conditions, as shown in foregoing sections, we arrive at even simpler form of the temperature variation of k_0^x at constant volume. We quite agree with Evans and Polanyi's view of referring measured E_A to constant pressure and of raising the importance of that at constant volume derivable therefrom for the theory of reaction in solution.

8. Application V. Heterogeneous reactions

8.1. Dependence of the rate on concentrations

We see from Eq. (5.14) that the rate of the heterogeneous elementary reaction varies proportional to p^{δ^1} or, as remarked in Section 6.1, to $\prod_i (N_i^{\delta_i^1})^{v_i^1}$ of the initial complex in the ideal homogeneous fluid provided $\Theta_{\sigma^*(0)}$ in Eq. (5.14) sufficiently approximates unity and hence $q_{\sigma^*}^{\delta^*}$ remains constant owing to the absence of interaction.

In the other extreme case when $\Theta_{\sigma^*(\delta^M)} \simeq 1$ or the surface is practically covered by adsorbed molecules δ^M 's, $q_{\sigma^*}^{\delta^*}$ may be taken constant, δ^* being surrounded by definite sort of molecules. The dependence of the rate on $N_i^{\delta_i^1}$'s as well as on $N_m^{\delta_m^M}$'s of molecules δ_m^M in homogeneous fluid, whose set,

$$\delta^M = \sum_m v_m^M \delta_m^M \quad (8.1)$$

is in equilibrium with adsorbed δ^M , is deduced as follows.

Rewriting $\Theta_{\sigma^*(0)}$ according to Eq. (2.5) in the form,

$$\Theta_{\sigma^*(0)} = \frac{QC_{\sigma^*(0)}}{QC_0} = \frac{QC_{\sigma^*(0)}}{QC_{\sigma^*(\delta^M)}} \frac{QC_{\sigma^*(\delta^M)}}{QC_0^{\delta^M}} \frac{QC_0^{\delta^M}}{QC_0},$$

and noting the relations Eqs. (2.2)–(2.4)

$$p^{\delta^M} = \frac{QC_0^{\delta^M}}{QC_0}, \quad q_{\sigma^*}^{\delta^M} = \frac{QC_{\sigma^*(\delta^M)}}{QC_{\sigma^*(0)}} \quad \text{and}$$

$$\Theta_{\sigma^*(\delta^M)} = \frac{QC_{\sigma^*(\delta^M)}}{QC_0^{\delta^M}},$$

we have

$$\Theta_{\sigma^*(0)} = \frac{p^{\delta^M}}{q_{\sigma^*}^{\delta^M}} \Theta_{\sigma^*(\delta^M)} \quad (8.2)$$

or substituting $\Theta_{\sigma^*(0)}$ from Eq. (8.2) in Eq. (5.14)

$$\bar{v}_1 = \kappa \frac{kT}{h} G_1 \frac{q_{\sigma^*}^{\delta^*} p^{\delta^M}}{q_{\sigma^*}^{\delta^M} p^{\delta^I}} \Theta_{\sigma^*(\delta^M)}. \quad (8.3)$$

We see now that if $\Theta_{\sigma^*(\delta^M)} = 1$, \bar{v} varies proportional to $p^{\delta^M}/p^{\delta^I}$, i.e.

$$\bar{v}_1 = \kappa \frac{kT}{h} G_1 \frac{q_{\sigma^*}^{\delta^*} p^{\delta^M}}{q_{\sigma^*}^{\delta^M} p^{\delta^I}}. \quad (8.4)$$

It follows that (I) the rate is proportional to $(N_i^{\delta^I})^{v_i^I}$ in the ideal homogeneous fluid according to Eqs. (3.5) and (5.7), and inversely proportional to $(N_m^{\delta^M})^{v_m^M}$ there.

If in latter case (II) it happens that δ_i^I 's and δ_m^M 's are individually identical to each other or that the initial complex δ^I itself exclusively occupies σ^* , the rate is independent of the concentration $N_i^{\delta^I}$'s or of $N_m^{\delta^M}$'s. If on the other hand (III) δ_i^I 's are partially identical to δ_m^M 's the conclusions (I) holds true with the remaining part of δ_i^I 's and δ_m^M 's.

The above reasoning about the effect of p^{δ^M} or $\prod^m (N_m^{\delta^M})^{v_m^M}$ on the rate affords the theory of the catalytic poison. Rather curious conclusion that the rate is inversely proportional to $\prod^m (N_m^{\delta^M})^{v_m^M}$ of δ^M , even when the latter nearly covers the catalyst, is correctly arrived at by Laidler et al. [33], who extended their theory treating the heterogeneous elementary reaction like a homogeneous one between sites and molecules.

8.2. The temperature variation of the rate

The temperature variation of \bar{v}_1 of the heterogeneous elementary reaction of the effusion type²⁵ is expressed according to Eq. (5.14a), as

$$RT^2 \frac{\partial \log \bar{v}_1}{\partial T} = RT + \Delta|^* \bar{E}_{\sigma^*} + \Delta|_{\sigma^*(0)}^{\theta} \bar{E}, \quad (8.5)$$

where

$$\Delta|^* \bar{E}_{\sigma^*} = \Delta|_{\sigma^*(\delta^*)}^q \bar{E} - \Delta|_{\delta^I}^p \bar{E}, \quad (8.6)$$

$$\Delta|_{\sigma^*(0)}^{\theta} \bar{E} = RT^2 \frac{\partial \log \Theta_{\sigma^*(0)}}{\partial T}, \quad (8.7.0)$$

$$\Delta|_{\sigma^*(\delta^*)}^q \bar{E} = RT^2 \frac{\partial \log q_{\sigma^*}^{\delta^*}}{\partial T} \quad (8.7.q)$$

and

$$\Delta|_{\delta^I}^p \bar{E} = RT^2 \frac{\partial \log p^{\delta^I}}{\partial T}. \quad (8.7.p)$$

$\Delta|_{\sigma^*(0)}^{\theta} \bar{E}$, $\Delta|_{\sigma^*(\delta^*)}^q \bar{E}$ and $\Delta|_{\delta^I}^p \bar{E}$ are according to Eq. (3.13) increments due to the process, respectively, associated with $\Theta_{\sigma^*(0)}$, $q_{\sigma^*}^{\delta^*}$ and p^{δ^I} , of the average energy \bar{E} or of the internal energy of the whole assembly, whose external parameters are fixed. $\Delta|^* \bar{E}_{\sigma^*}$ is hence according to Eq. (8.6) the increment caused by bringing δ^I from somewhere in the assembly into preliminarily evacuated σ^* to form δ^* there, the $\Delta|^*$'s are thus increments of internal energy or of enthalpy according as the assembly of interest is A_V or A_P , respectively.²⁶

The alternative expression of the temperature variation is obtained by differentiating Eq. (8.3) as

$$RT^2 \frac{\partial \log \bar{v}_1}{\partial T} = RT + \Delta|^* \bar{E}_{\sigma^*} + \Delta|^M \bar{E}_{\sigma^*} + \Delta|_{\sigma^*(\delta^M)}^{\theta} \bar{E}, \quad (8.8)$$

where

$$\Delta|^M \bar{E}_{\sigma^*} = \Delta|_{\delta^M}^p \bar{E} - \Delta|_{\sigma^*(\delta^M)}^q \bar{E}, \quad (8.9)$$

$$\Delta|_{\sigma^*(\delta^M)}^{\theta} \bar{E} = RT^2 \frac{\partial \log \Theta_{\sigma^*(\delta^M)}}{\partial T}, \quad (8.10.0)$$

$$\Delta|_{\delta^M}^p \bar{E} = RT^2 \frac{\partial \log p^{\delta^M}}{\partial T} \quad (8.10.p)$$

²⁵ cf. Section 7.2.

²⁶ cf. Section 3.9.

and

$$\Delta|_{\sigma^*(\delta^M)}^q \bar{E} = RT^2 \frac{\partial \log q_{\sigma^*}^{\delta^M}}{\partial T}. \quad (8.10.q)$$

The latter three quantities are, according to Eq. (3.13) increments due to the operation associated, respectively, with $\Theta_{\sigma^*(\delta^M)}$, p^{δ^M} and $q_{\sigma^*}^{\delta^M}$ of the average energy \bar{E} or the internal energy of the whole assembly whose external parameters are fixed. $\Delta|^M \bar{E}_{\sigma^*}$ is similarly as in the previous case such increment caused by bringing δ^M from somewhere in the assembly into σ^* . These increments are those of the internal energy or of the enthalpy of the interested assembly according as the latter is A_V or A_P .²⁷

If practically all of δ^M 's are situated in the homogeneous part of the assembly, $\Delta|^M \bar{E}_{\sigma^*}$ is identified with the heat of adsorption at constant volume or pressure, respectively, according as the assembly of interest is either A_V or A_P .

In the extreme case when $\Theta_{\sigma^*(0)} = 1$ or $\Theta_{\sigma^*(\delta^M)} = 1$, $\Delta|_{\sigma^*(0)}^{\theta} \bar{E}$ or $\Delta|_{\sigma^*(\delta^M)}^{\theta} \bar{E}$, respectively, vanishes according to Eq. (8.7.0) or Eq. (8.10.0) and hence Eq. (8.5) or Eq. (8.8) for $RT^2 \partial \log \bar{v}_1 / \partial T$ assumes, respectively, the form,

$$RT^2 \frac{\partial \log \bar{v}_1}{\partial T} = RT + \Delta|^* \bar{E}_{\sigma^*} \quad (8.11.I)$$

or

$$RT^2 \frac{\partial \log \bar{v}_1}{\partial T} = RT + \Delta|^* \bar{E}_{\sigma^*} + \Delta|^M \bar{E}_{\sigma^*}. \quad (8.11.II)$$

As to the relative magnitude of $RT^2 \partial \log \bar{v}_1 / \partial T$ at the both extremities and to the temperature region of their appearance, the following may be inferred assuming the relation of Eq. (4.12)²⁸

$$\theta = \Theta_{\sigma^*(\delta^M)} = 1 - \Theta_{\sigma^*(0)}. \quad (8.12)$$

Equating alternative forms of $RT^2 \partial \log \bar{v} / \partial T$, Eqs. (8.5) and (8.8), with due regard to Eqs. (8.7.0), (8.9) and (8.10.0), we have

$$RT^2 \frac{\partial \log \Theta_{\sigma^*(0)}}{\partial T} - RT^2 \frac{\partial \log \Theta_{\sigma^*(\delta^M)}}{\partial T} = \Delta|^M \bar{E}_{\sigma^*} \quad (8.13)$$

²⁷ cf. Section 3.9.

²⁸ This holds true when the states $\sigma^*(0)$ and $\sigma^*(\delta^M)$ are practically only possible alternative states of σ^* , $\Theta_{\sigma^*(\delta^*)}$ being thereby negligible (cf. Section 4.3).

or by Eq. (8.12)

$$RT^2 \frac{\partial \log (1 - \theta)}{\partial T} - RT^2 \frac{\partial \log \theta}{\partial T} = \Delta|^M \bar{E}_{\sigma^*}. \quad (8.14)$$

Eq. (8.14) shows, since $-RT^2(\partial \log \theta / \partial T)$ and $RT^2(\partial \log (1 - \theta) / \partial T)$ are necessarily of equal sign, that θ increases or decreases with increasing temperature according as $\Delta|^M \bar{E}_{\sigma^*}$ is negative or positive, respectively. Provided that the latter is at least approximately constant, the extreme cases $\theta = 0$ and $\theta = 1$ should hence, respectively, appear at lower and higher extremities of temperature or reverse according as $\Delta|^M \bar{E}_{\sigma^*}$ is negative or positive, as shown by the scheme,

$\Delta ^M \bar{E}_{\sigma^*}$	$\theta \rightarrow 0$	$\theta \rightarrow 1$
neg.	Temp, lower	Temp, higher
pos.	Temp, higher	Temp, lower

On the other hand, Eq. (8.11) show that $RT^2(\partial \log \bar{v}_1 / \partial T) = E_H$ is greater at $\theta = 0$ than at $\theta = 1$ or reversed according as $\Delta|^M \bar{E}_{\sigma^*}$ is negative or positive as shown by the scheme,

$\Delta ^M \bar{E}_{\sigma^*}$	$\theta \rightarrow 0$	$\theta \rightarrow 1$
neg.	E_H greater	E_H smaller
pos.	E_H smaller	E_H greater

We see readily, overlapping above two schemes, that E_H is always greater at the lower extremity of temperature than at the higher.

$\log \bar{v}_1$, may hence vary linearly with $1/RT$, respectively, at the extremities, the inclination gradually decreasing over the transient region by the amount $|\Delta|^M \bar{E}_{\sigma^*}|$ with increasing temperature. In the case when $\Delta|^* \bar{E}_{\sigma^*}$ and $\Delta|^M \bar{E}_{\sigma^*}$ differ in sign and $|\Delta|^* \bar{E}_{\sigma^*}| < |\Delta|^M \bar{E}_{\sigma^*}|$, the rate will have a maximum or an optimum temperature in the transient region. If we exclude the possibility that $\Theta_{\sigma^*(\delta^M)} = 1$ at higher extremity of temperature,²⁹ only possible case is that

²⁹ Provided that δ^M forms a single molecule in the homogeneous fluid, we have according to Eqs. (4.15) and (8.14)

$$\Delta|^M \bar{E}_{\sigma^*} = N_A \varepsilon_{\sigma^*}.$$

Eq. (4.15) shows on the other hand that θ increases with increasing temperature, when $\Delta|^M \bar{E}_{\sigma^*}$ or ε_{σ^*} is negative, but θ may approximate unity only when $|\sigma|N^{\delta^M} \gg 1$ or δ^M in the homogeneous fluid is far more concentrated than at saturation on the boundary, a situation which can hardly be realized.

$\Delta^M \bar{E}_{\sigma^*} > 0$ and $\Theta_{\sigma^*(\delta^M)} = 0$ or 1, respectively, at higher or lower extremity of temperature.

The two extreme cases corresponding to Eq. (8.11) are recognized by Hinshelwood [34] who treats the heterogeneous elementary reaction in extension of the theory of homogeneous one, in terms of “the rate constant k' ” and of “the apparent heat of activation $RT^2(\partial \log k'/\partial T)$ of the heterogeneous reaction.” Hinshelwood arrives by several assumptions and approximations at the relation for the case $\theta = 0$ that the “apparent heat of activation, $RT^2(\partial \log k'/\partial T)$ ” equals “the true heat of activation” minus “the energy of desorption.” The “true heat of activation” is according to him the heat required to bring up an adsorbed reaction complex to the critical complex and the “energy of desorption” the heat required to set the adsorbed reaction complex free. His apparent heat of activation equals, however $RT^2(\partial \log \bar{v}_1/\partial T)$, provided that the “rate constant” is determined at constant N^{δ^i} 's throughout a range of temperature as is usually done, since he defines the “rate constant” as the ratio of the rate to $\prod^i (N^{\delta^i})^{v_i}$ in a homogeneous fluid. Hence, $RT^2(\partial \log k'/\partial T)$ or $RT^2(\partial \log \bar{v}_1/\partial T)$ at $\theta = 0$ which equals except the minor term RT^{30} the increment of \bar{E} or of U caused by bringing the initial complex to the critical state in σ^* according to Eq. (8.11.I)³¹, may simply be divided, if one prefers as did by Hinshelwood, in two parts, i.e. that due to the process of bringing the initial complex simply into σ^* or negative “energy of desorption” and that of raising the initial complex there to the critical complex provided that initial complexes are situated practically exclusively in the homogeneous fluid.

For the case when $\Theta_{\sigma^*(\delta^M)} = 1$ Hinshelwood similarly arrives at an expression equating $RT^2(\partial \log k'/\partial T)$ to the sum of the “apparent heat of activation” and the “energy of desorption” of “retarding gas.” This conforms again with Eq. (8.11.II)

³⁰ Since the statistical average of kinetic energy of the mode of motion normal to the critical surface amounts just to RT if reckoned per mol of the critical complex [35], the right-hand side of Eq. (8.11.I) gives the increment of \bar{E} reckoned per mol of reacting complex caused by bringing the initial over into the critical complex transiting the critical surface.

³¹ If $\theta \neq 0$ or σ^* is not preliminarily evacuated with certainty, the latter process must be associated with the more or less additional increment for clearing up σ^* which amounts as much as to $\Delta^M \bar{E}_{\sigma^*}$ in the extreme case of Eq. (8.11.II) when $\theta = 1$.

since the “energy of desorption” of the “retarding gas” exactly corresponds to $\Delta^M \bar{E}_{\sigma^*}$ of δ^M .

We see, however, no advantage to force the rate constant method of the homogeneous elementary reaction into the heterogeneous reaction, where the “rate constant” is in general by no means a constant, and to detail the picture so that the initial complex preliminarily assumes the state what is called adsorbed at σ^* before making the critical complex there. We should rather, specialize the use of the rate constant and its temperature variation duly to the homogeneous elementary reaction and deal directly with \bar{v}_1 and $RT^2(\partial \log \bar{v}_1/\partial T)$ without introducing the intermediate state, which may even be fictitious.

8.3. The rate expression allowed for the mutual interaction among adsorbed molecules

We will now formulate the rate of the heterogeneous elementary reaction allowing for the mutual interaction among adsorbed molecules with an example of the catalytic atomization of hydrogen on the surface of a metallic catalyst.

Our assembly will consist of a metallic catalyst in the hydrogen atmosphere, where the catalysed dissociation of hydrogen molecules is going on, each of them changing into a pair of adsorbed hydrogen atoms. Metal atoms of our catalyst are allayed as in Section 4.6 on a plane square pattern, each affording one of identical sites σ 's for an adsorbed hydrogen atom whereas each adjacent pair proving σ^* for the critical complex H_2^* , which consists of two hydrogen atoms.

Expressing p^{δ^I} of the initial complex δ^I according to Eq. (3.5) in the form,

$$p^{\delta^I} = \frac{Q_{H_2}}{N_{H_2}} \quad (8.15)$$

and p^{δ^F} of δ^F , which consist of two hydrogen atoms, according to Eq. (2.11) in the form,

$$p^{\delta^F} = (p^H)^2, \quad (8.16)$$

we have according to Eq. (5.14)

$$\bar{v}_1 = \kappa \frac{kT}{h} G_1 q_{\sigma^*}^{H_2^*} \Theta_{\sigma^*(0)} \frac{N_{H_2}}{Q_{H_2}}, \quad (8.17a)$$

$$\bar{v}_1 = \kappa \frac{kT}{h} G_1 q_{\sigma^*}^{H_2^*} \Theta_{\sigma^*(0)} (p^H)^{-2}. \quad (8.17b)$$

These expressions for the rate will be developed into the form accessible to the numerical calculation taking the mutual interaction among adsorbed molecules into account, but neglecting that between lattices and molecules in the homogeneous fluid and assuming that any site σ is either occupied by H or else vacant, i.e.

$$\theta = \Theta_{\sigma(\text{H})} = 1 - \Theta_{\sigma(0)}. \quad (8.18)$$

For the first approximation it is assumed that the additional reversible work³² required to bring up a hydrogen atom or the critical complex to a site due to surrounding adsorbed hydrogen atoms is proportional to their degree of adsorption θ , i.e.

$$-RT \log q_{\sigma}^{\text{H}} = -RT \log q_{\sigma,0}^{\text{H}} + \theta \omega \quad (8.19.H)$$

and

$$-RT \log q_{\sigma^*}^{\text{H}_2^*} = -RT \log q_{\sigma^*,0}^{\text{H}_2^*} + \theta \omega^*, \quad (8.19.H2)$$

where $-RT \log q_{\sigma,0}^{\text{H}}$ or $-RT \log q_{\sigma^*,0}^{\text{H}_2^*}$ is the reversible work reckoned per mol required, in the absence of interaction, to bring up a hydrogen atom or a reaction complex from its standard state into σ forming an adsorbed hydrogen atom or a critical complex, respectively, there, $\theta \omega$ or $\theta \omega^*$ being the additional reversible work due to the interaction taken proportional to θ .

Assuming further

$$\Theta_{\sigma^*(0)} = (1 - \theta)^2, \quad (8.20)$$

we have from Eqs. (8.17a), (8.19.H2) and (8.20)

$$\vec{v}_1 = \kappa \frac{kT}{h} G_1 \frac{q_{\sigma^*,0}^{\text{H}_2^*}}{Q_{\text{H}_2}} e^{-\theta \omega^*/RT} N^{\text{H}_2} (1 - \theta)^2. \quad (8.21)$$

Eq. (8.21) gives the rate as a function of θ and N^{H_2} .

Expressing p^{H} , on the other hand, in the form,

$$p^{\text{H}} = \frac{1 - \theta}{\theta} q_{\sigma}^{\text{H}} \quad (8.22)$$

according to Eqs. (3.1) and (8.18), we have by Eqs. (8.17b), (8.19.H2), (8.20) and (8.22) for the rate \vec{v} of the reverse elementary reaction

$$\vec{v}_1 = \kappa \frac{kT}{h} G_1 \frac{q_{\sigma^*,0}^{\text{H}_2^*}}{(q_{\sigma,0}^{\text{H}})^2} e^{-(\omega^* - 2\omega)\theta/RT} \theta^2. \quad (8.23)$$

The reverse rate is thus a function solely of θ .

³² cf. Section 3.3.

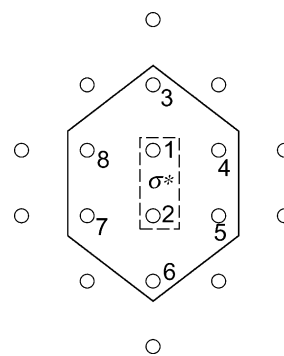


Fig. 1.

The above procedure of allowing for the mutual interaction is applied to the theory of hydrogen electrode process on nickel, with the rate-determining step of the catalysed atomization of hydrogen by Okamoto, Horiuti and Hirota [1], who arrive at semi-quantitative explanation of the process especially of Tafel's empirical rule [36,37].

We now calculate the rate excluding the latter approximations but assuming instead that the interaction between hydrogen atoms including those of critical complex is significant only between directly neighbouring ones.

We consider our assembly $C_{\Sigma(0)}$ at a particular state, that a group Σ of sites consisting of particular σ^* and its direct neighbours shown enclosed by full lines in Fig. 1, are unoccupied. The sites belonging to Σ are numbered as shown by annexed figures in Fig. 1.

We now proceed to calculate, with reference to $QC_{\Sigma(0)}$, $q_{\sigma^*}^{\delta^*} \Theta_{\sigma^*(0)}$ in Eqs. (8.17a) and (8.17b) which is expressed according to Eqs. (2.3) and (2.5) as

$$q_{\sigma^*}^{\text{H}_2^*} \Theta_{\sigma^*(0)} = \frac{QC_{\sigma^*(\text{H}_2^*)}^{\text{H}_2^*}}{QC_0}. \quad (8.24)$$

$QC_{\sigma^*(\text{H}_2^*)}^{\text{H}_2^*}$ is given similarly as in Section 4.6, by

$$QC_{\sigma^*(\text{H}_2^*)}^{\text{H}_2^*} = QC_{\Sigma(0)}^{\text{H}_2^*} q_{\sigma^*,0}^{\text{H}_2^*} \sum_{\theta_3, \dots, \theta_8} \left(\frac{q_{\sigma,0}^{\text{H}}}{p^{\text{H}}} \xi^* \right)^{\theta_3 + \dots + \theta_8} \times \eta_3^{\theta_3 + \theta_6} \eta_4^{\theta_4 + \theta_5 + \theta_7 + \theta_8} \xi^{\theta_4 \theta_5 + \theta_7 \theta_8}, \quad (8.25)$$

where η 's of the sites σ_3 and σ_6 on the one hand, and of σ_4 , σ_5 , σ_7 , and σ_8 and on the other hand are taken, respectively, identical with each other, because of the symmetry of the figure.

QC_0 is given by

$$QC_0 = QC_{\Sigma(0)} \sum_{\theta_1, \dots, \theta_8} \left(\frac{q_{\sigma,0}^H}{p^H} \right)^{\theta_1 + \dots + \theta_8} \times \eta_3^{\theta_3 + \theta_6} \eta_4^{\theta_4 + \theta_5 + \theta_7 + \theta_8} \times \xi^{\theta_4 \theta_5 + \theta_7 \theta_8 + \theta_1(\theta_3 + \theta_4 + \theta_2 + \theta_8) + \theta_2(\theta_5 + \theta_6 + \theta_7)}. \quad (8.26)$$

By Eqs. (8.24)–(8.26) we have now

$$q_{\sigma^*}^{H_2} \Theta_{\sigma^*(0)} = \frac{q_{\sigma^*,0}^{H_2} \sum_{\theta_3, \dots, \theta_8} (q_{\sigma,0}^H \xi^*/p^H)^{\theta_3 + \dots + \theta_8} \eta_3^{\theta_3 + \theta_6} \eta_4^{\theta_4 + \theta_5 + \theta_7 + \theta_8} \xi^{\theta_4 \theta_5 + \theta_7 \theta_8}}{\sum_{\theta_1, \dots, \theta_8} (q_{\sigma,0}^H/p^H)^{\theta_1 + \dots + \theta_8} \eta_3^{\theta_3 + \theta_6} \eta_4^{\theta_4 + \theta_5 + \theta_7 + \theta_8} \xi^{\theta_4 \theta_5 + \theta_7 \theta_8 + \theta_1(\theta_3 + \theta_4 + \theta_2 + \theta_8) + \theta_2(\theta_5 + \theta_6 + \theta_7)}}, \quad (8.27)$$

For unknown constants η_3 and η_4 we have on the other hand the relation,

$$QC_{\sigma_1(0)} = QC_{\sigma_3(0)} = QC_{\sigma_4(0)} \quad (8.28)$$

as in Section 4.6, because of physical identity of σ_1 , σ_3 and σ_4 .

$QC_{\sigma_1(0)}$, $QC_{\sigma_3(0)}$, or $QC_{\sigma_4(0)}$ is, respectively, obtained by putting θ_1 , θ_3 , or θ_4 in Eq. (8.26) at zero.

$QC_{\sigma_1(0)}$ in Eq. (8.28) and QC_0 in Eq. (8.26) are on the other hand related to θ according to Eqs. (2.5) and (8.18) by

$$1 - \theta = \frac{QC_{\sigma_1}}{QC_0}. \quad (8.29)$$

Substituting now $q_{\sigma^*}^{H_2} \Theta_{\sigma^*(0)}$ from Eq. (8.27) into Eq. (8.17a) or Eq. (8.17b) and eliminating p^H , η_3 and η_4 therefrom by Eqs. (8.28) and (8.29), we have the expression for \vec{v}_1 as the function of N^{H_2} and θ or that for \vec{v}_1 as the function of θ , respectively.

Remembering now two of sites are occupied anew as the result of one act of the catalysed dissociation, the overall increasing rate of adsorbed hydrogen atoms is given by

$$G_1 \frac{d\theta}{dt} = 2(\vec{v}_1 - \tilde{v}_1), \quad (8.30)$$

or by integration,

$$\frac{G_1}{2} \int_{\theta_1}^{\theta_2} \frac{d\theta}{\vec{v}_1 - \tilde{v}_1} = t_2 - t_1, \quad (8.31)$$

where θ_1 , and θ_2 are, respectively, the degree of adsorption at the time t_1 and t_2 . Substituting \vec{v}_1 , and \tilde{v}_1 of either approximation and estimating κ , G , $q_{\sigma^*,0}^{H_2}$, $q_{\sigma,0}^H$, ω^* , ω , ξ^* and ξ properly, we have the relation between θ and t accessible to the experimental verification.

Actual calculation and its experimental verification will be presented in a later paper.

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