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Title	A Method of Statistical Mechanical Treatment of Equilibrium and Chemical Reaction.
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Citation	觸媒, 3, 92-102
Issue Date	1948-01
Doc URL	https://hdl.handle.net/2115/30396
Type	departmental bulletin paper
File Information	3_P92-102.pdf



A Method of Statistical Mechanical Treatment of Equilibrium and Chemical Reaction.

(Abstract)

By Juro Horiuti

A method is proposed for treating equilibrium and chemical reaction by means of a set of four conjugate functions in extension of an earlier method applied to the hydrogen electrode process.⁽¹⁾ The basic assumption for the method is that the behavior of a certain macroscopic assembly is described in terms of an appropriate quantum canonical ensemble. Such assembly is called at statistical equilibrium. These functions are,

$$p^\delta = \frac{\Omega C_0^\delta}{\Omega C_0}, \quad q_{\sigma^\delta} = \frac{\Omega C_{\sigma^\delta}^\delta}{\Omega C_{\sigma(0)}}, \quad \theta_{\sigma(\delta)} = \frac{\Omega C_{\sigma^\delta}^\delta}{\Omega C_0^\delta}, \quad \theta_{\sigma(0)} = \frac{\Omega C_{\sigma(0)}}{\Omega C_0} \quad (1)$$

where ΩC 's are the partition functions of interested macroscopic assembly, whose sets of eigen values and hence their partition functions are defined by respective sets of parameters. The parameters expressed in terms of macroscopic quantities, such as volume of external field strength are called here external parameters and those of microscopic ones defining a certain microscopic state of C the internal parameters. C_0 is now the assembly without any constraints on internal parameters. C_0^δ is that derived from C_0 by admitting a microscopic system δ with external parameters fixed but internal ones unconstrained $C_{\sigma(0)}$ that by imposing upon C_0 the microscopic constraint that σ , a certain quantum state of a microscopic cavity to hold δ , is vacant with certainty and $C_{\sigma(\delta)}^\delta$ that by imposing upon C_0^δ the constraint that σ is occupied by δ . $\theta_{\sigma(\delta)}$ or $\theta_{\sigma(0)}$ has thus the physical meaning of probability that σ is occupied by δ or vacant.

Theorems are derived from the definitions as follows.

$$(I) \quad q_{\sigma^\delta} = \frac{\theta_{\sigma(\delta)}}{\theta_{\sigma(0)}} p^\delta \text{ and consequently } p^\delta = \frac{Q^\delta}{N^\delta} \quad (2\cdot a)(2\cdot b)$$

where $Q^\delta = \lim_{|\sigma| \rightarrow 0} \frac{q_{\sigma^\delta}}{|\sigma|}$, $N^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\theta_{\sigma(\delta)}}{|\sigma|}$ and $|\sigma|$ the size of a microscopic cavity. For homogeneous assembly Q^δ is constant all over its extension and N^δ is thereby the concentration of δ . For a perfect gas assembly Q^δ is the ordinary partition function of a single molecule moving in a unit volume and a function only of temperature.

(1) Okamoto, Horiuti & Hirota; Sc. Pap. Inst. Phys. Chem. Res. Tokio, **39** (1933), 223.

(II) If a group of systems $\delta^A = \sum_a \nu^A_a \delta^A_a$ in the assembly is allowed under the proscribed constraints on the parameters to assume other state of aggregation $\delta^B = \sum_b \nu^B_b \delta^B_b$ etc., we have,

$$p^{\delta^A} = p^{\delta^B} = \dots \quad (3.a)$$

where

$$p^{\delta^A} = \prod_a (p^{\delta^A_a})^{\nu^A_a}, \quad p^{\delta^B} = \prod_b (p^{\delta^B_b})^{\nu^B_b}, \dots \quad (3.b)$$

and ν^A_a or ν^B_b denotes respective number of members δ^A_a or δ^B_b of δ^A or δ^B . δ^A and δ^B in such a relation are called in equilibrium with each other.

(III) $-kT \log \lambda$ is the work required to carry out the operation associated with λ , which represents the four functions, keeping the whole assembly at statistical-equilibrium throughout: $-kT \log p^{\delta}$ is thus the work required to bring up δ from its standard state into C_a , $-kT \log q^{\delta}_\sigma$ that into preliminarily evacuated σ of $C_{\sigma(0)}$ and $-kT \log \theta_{\sigma(0)}$ or $-kT \log \theta_{\sigma(0)}$ that to clear up or fill up σ with δ respectively. $-RT \log p^{\delta}$ in particular is denoted as that,

$$\mu^{\delta} = -RT \log p^{\delta} \quad (4)$$

and is called the chemical potential of δ .

$$(IV) \quad -kT \log \lambda = \Delta_\lambda F \quad (5)$$

where $\Delta_\lambda F$ is the increment of F called the free energy and defined by,

$$F = -kT \log \Omega C \quad (6)$$

due to the operation associated with λ . The C in Eq. (6) represents C , $C_{\sigma(0)}$ and $C_{\sigma(s)}$. Increment of F is in general equals the work required to produce the corresponding change in parameters keeping the whole assembly at statistical equilibrium.

$$(V) \quad kT^2 \frac{\partial \log \lambda}{\partial T} = \Delta_\lambda U \quad (7)$$

where the partial differentiation and the increment are referred to the fixed external parameters and U the statistical average of eigenvalues called the internal energy hereafter. By Eq. (5) and (7) we have,

$$\Delta_\lambda F - T \frac{\partial \Delta_\lambda F}{\partial T} = \Delta_\lambda U \quad (8)$$

(VI) $-kT \log \lambda$ is alternatively expressed in the form,

$$-kT \log \lambda = (\Delta_\lambda Z)_\pi \quad (9)$$

where

$$Z = F + \sum_a \Pi_{\alpha_a} \alpha_a \quad (10)$$

α_a 's are the external parameters and $\Pi_{\alpha_a} = \frac{\partial kT \log \Omega C}{\partial \alpha_a}$ which proved to be the statistical average force exerted by C to increase α_a . The partial differentiation with suffix Π is referred to constant Π_{α_a} 's. Π_{α_a} is called hereafter the force conjugated with α_a .

$$(VII) \quad kT^2 \left(\frac{\partial \log \lambda}{\partial T} \right)_{\pi} = (\Delta_{\lambda} X)_{\pi} = (\Delta_{\lambda} Z)_{\pi} - T \left\{ \frac{\partial (\Delta_{\lambda} Z)_{\pi}}{\partial T} \right\}_{\pi} \quad (11)$$

where

$$X = U + \sum_a \Pi_{a\alpha} \alpha_a$$

Defining entropy by $S = -\frac{\partial F}{\partial T}$, we have

$$S = -\frac{\partial F}{\partial T} = -\left(\frac{\partial Z}{\partial T} \right)_{\pi},$$

$$\Delta_{\lambda} F = \Delta_{\lambda} Z = \Delta_{\lambda} U - T \Delta_{\lambda} S = (\Delta_{\lambda} X)_{\pi} - T (\Delta_{\lambda} S)_{\pi} \quad (12)$$

(VIII) In the special case when $\lambda = p^{\delta}$ and the volume is only external parameter, we have,

$$X = U + PV \quad (13)$$

$$\mu^{\delta} = \bar{F}_v^{\delta} = \bar{Z}_p^{\delta} = \bar{U}_v^{\delta} - T \bar{S}_v^{\delta} = \bar{X}_p^{\delta} - T \bar{S}_p^{\delta} \quad (14)$$

and

$$S_{\delta v} = \left(\frac{\partial \mu^{\delta}}{\partial T} \right), \quad \bar{S}_p^{\delta} = \left(\frac{\partial \mu^{\delta}}{\partial T} \right) \quad (15V), (15)$$

$$\left(\frac{\partial \mu^{\delta}}{\partial p} \right)_T = V_{\delta p} \quad (16)$$

where P is the pressure or the force conjugated with volume, N_A Avogadro's number and

$$\bar{Q}_{v_f}^{\delta} = N_A (\Delta_p Q)_v \quad \text{or} \quad \bar{Q}_p^{\delta} = N_A (\Delta_p Q)_p$$

is the partial molal quantity.

Application to Equilibrium

(1) Mean population or the distribution function f_s of the quantum state σ_s of the individual constituent system of the assembly is expressed as that,

$$f_s = \frac{0 \times \theta_{\sigma_s(0)} + 1 \times \theta_{\sigma_s(\delta)} + 2 \times \theta_{\sigma_s(2\delta)} \cdots + \nu \theta_{\sigma_s(\nu\delta)} \cdots}{\theta_{\sigma_s(0)} + \theta_{\sigma_s(\delta)} + \theta_{\sigma_s(2\delta)} \cdots + \theta_{\sigma_s(\nu\delta)} \cdots}$$

where ν is the number of δ 's simultaneously occupying σ_s and $\theta_{\sigma_s(\nu\delta)}$ the corresponding probability.

It is further derived that $\theta_{\sigma(\nu\delta)}/\theta_{\sigma(0)} = \{\theta_{\sigma_s(\delta)}/\theta_{\sigma_s(0)}\}^{\nu}$, and that $q_{\sigma}^{\delta} = e^{-\frac{\epsilon_s}{kT}}$ where ϵ_s is the eigenvalue of σ_s state. Allowing for any number of δ to occupy σ in accordance with the symmetric wave function of the assembly we have by Eq. (2a), (4) and above three ones, $f_s = (e^{\frac{\epsilon_{\sigma(0)} - \mu^{\delta}}{kT}} - 1)^{-1}$ or the f_s for the Bose-Einstein statistics. Putting on the other hand $\theta_{\sigma_s(\nu\delta)} = 0$ for $\nu > 2$ in accordance with antisymmetric wave function we have $f_s = (e^{\frac{\epsilon_{\sigma(0)} - \mu^{\delta}}{kT}} + 1)^{-1}$ or that of Fermi-Dirac statistics.

(2) The equilibrium constant K_N for the homogeneous assembly is obtained from Eqs.

$$(3) \text{ and } (2b) \text{ as that, } K_N = \prod (N^{\delta B_b})^{\nu B_b} / \prod (N^{\delta A_a})^{\nu A_a} = \prod (Q^{\delta B_b})^{\nu B_b} / (Q^{\delta A_a})^{\nu A_a}$$

(3) Simple adsorption isotherm for a pure gas is obtained from Eqs. (2a) identifying σ to the cite of adsorption, hence $\Theta_{\sigma(\delta)}$ to degree θ of adsorption, $\Theta_{\sigma(0)}$ to $1-\theta$ and p^δ to $\frac{Q^\delta}{N^\delta}$ of the gas according to Eqs. (2b) and (3b), as that $\frac{\theta}{1-\theta} = \frac{q^\delta_\sigma}{Q^\delta} N^\delta$. In the case of no interaction between adsorbed systems q^δ_σ is constant according to (III) independent of θ . Langmuir's adsorption isotherm thus being obtained.

(4) The result of 3) is immediately extended to the case of gas mixture with due regard to the relation, $\sum_g \Theta_{\sigma(\delta g)} + \Theta_{\sigma(0)} = 1$, where g signifies individual component gas.

(5) Allowing for the interaction between systems adsorbed on a net plane of cites the adsorption isotherm for a pure gas is derived as follows. We denote by $\Omega C_{\Sigma(0)}$ the partition function of the assembly, consisting of the adsorbent and the gas which has such a group of cites Σ unoccupied, as consisting of a particular cite σ , and so many surrounding cites σ_i 's as the force between δ there and that on δ is significant. The σ_i 's may be divided into several symmetry groups, $1 \dots s$, relevant respectively to different symmetry operations for cites around the center of the Σ . If we transfer an adsorbed system δ from outside Σ to a cite inside the latter, the partition function of the assembly becomes $\Omega C_{\Sigma(0)} \frac{q^\delta_\sigma}{p^\delta}$, where $q^\delta_\sigma = q^\delta_{\sigma,0} \eta_\sigma$, $q^\delta_{\sigma,0}$ the particular value of q^δ_σ in the absence of the interaction and η_σ the Boltzmann factor $e^{-\frac{\omega_\sigma}{kT}}$ of the additional work ω_σ due to the interaction with δ_σ 's situated outside Σ . (Cf. III). The q^δ_σ of δ brought further into Σ has another Boltzmann factor ξ of the additional work due to the interaction between the δ and the preoccupant. Constructing thus the partition function of the assembly for every possible mode of occupation of Σ and summing them up together we have ΩC_0 and picking up those terms consistent with the constraint $\sigma_0(0)$, $\sigma_0(\delta)$ or $\sigma_s(0)$'s, we have respectively $\Omega C_{\sigma_0(0)}$, $\Omega C_{\sigma_0(\delta)}$ or $\Omega C_{\sigma_s(0)}$'s in terms of p^{σ_0} , $q^{\sigma_0}_{\sigma_0}$, η_σ 's and ξ 's with the common factor $\Omega C_{\Sigma(0)}$.

We have now $\theta = \frac{\Omega C_{\sigma_0(\delta)}}{\Omega C_0}$ and $\Omega C_{\sigma_0(0)} = \Omega C_{\sigma_1(0)} = \dots = \Omega C_{\sigma_s(0)}$ according to Bethe and Peierls⁽²⁾ idea that σ_0 and σ_s 's are by no means physically different. Expressing p^δ for adsorbed δ according to Eqs. (2b) and (3a) as that $p^\delta = \frac{Q^\delta}{N^\delta}$ and properly estimating $q^\delta_{\sigma,0}$ and ξ 's, we have θ as a function of N^δ eliminating $\eta_1 \dots, \eta_s$ from above $s+1$ equations.

(2) Bethe; Proc. Roy. Soc. London, A150 (1935), 552.

Peierls; Proc. Cambridge Phil. Soc. 32 (1936), 471.

Application to Chemical Reaction

In this application we are interested in the assembly not necessarily in complete equilibrium. We consider an assembly resulting from the interested one by leaving the latter with fixed external parameters for infinite time. The canonical ensemble of the latter will partly have the momentary chemical composition of the original assembly. The basic assumption of the present application is now that the behavior of the interested assembly is described by that appropriate part of the ensemble. Such assembly is called in thermal equilibrium. λ 's are defined in terms of that part of the ensemble. On this basis the rate of the elementary reaction $\vec{v}$ and $\overleftarrow{v}$ in forward and backward direction are derived as a classical approximation in the form, ⁽³⁾⁽⁴⁾

$$\vec{v} = \kappa \frac{kT}{h} \frac{\Omega C_0^{\delta^*}}{\Omega C_0^{\delta^I}}, \quad \overleftarrow{v} = \kappa \frac{kT}{h} \frac{\Omega C_0^{\delta^*}}{\Omega C_0^{\delta^F}}$$

or according to the definition of p^{δ} 's.

$$\vec{v} = \kappa \frac{kT}{h} \frac{p^{\delta^*}}{p^{\delta^I}}, \quad \overleftarrow{v} = \kappa \frac{kT}{h} \frac{p^{\delta^*}}{p^{\delta^F}} \quad (17a) \quad (17b)$$

$C_0^{\delta^I}$ or $C_0^{\delta^F}$ consists of an assembly C_0 of a definite chemical composition augmented with the initial δ^I or the final δ^F complex, $C_0^{\delta^*}$ consists of C_0 and an additional set of elementary reaction or the reaction complex δ with its representative point constrained on a critical surface which separates the region of the configuration space of $C\delta$ corresponding to the state of initial complex of δ from that of the final complex and traversed by the minimum number of representative points in the space. The κ is the fraction of the representative points which complete the elementary reaction in one direction over those traversing the critical surface in either direction. The δ at the particular configuration or δ^* is called the critical complex. The derivation is not based on the assumption of equilibrium between δ^I and δ^* , dynamical independency of δ , the existence of the saddle point of the potential energy nor of its being determinant of the rate as in the case of transition state method.⁽⁵⁾⁽⁶⁾ The latter is included as the special case of present method.

Several applications of the expressions are developed as below.

(i) Let one event of the over-all reaction involves r those of the rate-determining step or the ratio of the resultant rate $\vec{v} - \overleftarrow{v}$ of the rate-determining step to the over-all rate v of a steady reaction be n.l.e.

(3) Horiuti; Bul. Chem. Soc. Japan **15** (1938), 210.

(4) Hirota & Horiuti; Sc. Pap. I.P.C.R. Tokio **94** (1938), 1174.

(5) Eyring; J. Chem. Phys. **3** (1935), 107.

(6) Evans & Polanyi; Trans. Faraday Soc. **31** (1935), 875.

$$n\vec{v} = \vec{v} - \overleftarrow{v} \quad (18)$$

For the reaction $2H^+ \rightarrow 2H \rightarrow H_2$ n is 2 or 1 according as the first or the second step is rate-determining. Since any elementary reaction but the rate-determining step is in equilibrium and hence does not affect the partition function of the whole assembly, by its occurrence according to Eq. 3, we have $p^{\delta R}/p^{\delta L} = (p^{\delta F}/p^{\delta I})^n$ or according to Eqs. (4), (17) and (18) $\vec{v}/\overleftarrow{v} = 1 - e^{-\frac{\mu_{\delta R} - \mu_{\delta L}}{nRT}}$, where δ^R or δ^L is the reaction or resultant of the over-all reaction and $\vec{v} = \overrightarrow{v}/n$ the number of δ^I passing over into δ^R unidirectionally per unit time. The $\vec{v}$, $\overleftarrow{v}$ and $\mu^{\delta R} - \mu^{\delta L}$ being measurable, $\vec{v}$ perhaps by means of isotopes, n may be experimentally determined.⁽⁷⁾ The present author proposes n , which might be called stoichiometrical number, as a more fundamental criterion for the reaction mechanism than the order of reaction which latter gives sometimes, especially in the case of heterogeneous reaction, only unsatisfactory knowledge.

(ii) For a homogeneous assembly Eqs. (17a) is conveniently transformed as that,

$$\vec{v}_1 = \frac{\overrightarrow{v}}{V} = \kappa \frac{kT}{h} Q^{s*} \prod_i \left(\frac{N_i^{\delta I}}{Q_i^{\delta I}} \right)^{\nu_i I} \quad (19)$$

or that

$$\kappa = \frac{\vec{v}_1}{\prod_i (N_i^{\delta I})^{\nu_i I}} = \kappa \frac{kT}{h} \frac{Q^{s*}}{\prod_i (Q_i^{\delta I})^{\nu_i I}} \quad (20)$$

Eq. (20) is of identical form with that of transition state method and even in contents provided the critical surface happens to pass through the saddle point perpendicular to the "reaction path."

It follows that the equilibrium assumption of the transition state method is not necessary for the final expression and hence all criticism against the method because of the assumption are invalidated. This does not of course mean that the equilibrium relation is justified. It is shown that the number of the reaction complex passing through the critical surface from the initial to the final region remains the same whether the elementary reaction is in equilibrium or not if $\kappa=1$, but the number is more or less reduced by passing from the elementary reaction in equilibrium to that proceeding irreversibly if $\kappa < 1$ ⁽³⁾⁽⁴⁾. In this sense equilibrium relation is justified only in the former case.

In general $\kappa=1$ when the representative point get straight forward through the neighbourhood of the critical surface without changing the momentum normal to the surface whereas $\kappa < 1$ when the momentum changes sign very frequently there. The former type is called

(7) Horiuti & Ikusima: Proc. Imp. Acad. Tokio **15** (1935), 39.

by the present author the effusion type and the latter the diffusion type,^{(3) (4)} Arrhenius⁽⁸⁾ and recently Eyring, Evans and Polanyi seem to follow the former picture on one hand and Nernst⁽⁹⁾ and recently Rabinowitch,⁽¹⁰⁾ Christiansen⁽¹¹⁾ and Norish⁽¹²⁾ the latter on the other hand. All existing data are however fitted sufficiently by the former. Forthcoming of experimental data is desired which are exclusively fitted by the latter thus leading us to the correct synthesis of these antithesis.

(iii) Basic assumption for the present application and the thermodynamical terminology developed in (III) to (VII) in terms of canonical ensemble enables us the following thermodynamical presentation of the rate expression. Assuming the volume only external parameter and defining the critical increment of a quantity M as that,

$$\Delta^* M_V = \bar{M}_V^{\circ*} - \sum_i \nu_i^I \bar{M}_{V_i}^{\circ I}, \quad \Delta^* M_P = \bar{M}_P^{\circ*} - \sum_i \nu_i^I \bar{M}_{P_i}^{\circ I} \quad (21)$$

i.e. as the increment of M due to bringing the reaction complex from the state of initial to that of the critical complex keeping V or P of the assembly constant, the rate $\vec{v}$ is expressed according to that Eqs. (17), (4) and (14) in the form,

$$\vec{v} = \kappa \frac{kT}{h} e^{-\frac{\Delta^* F_V}{RT}} = \kappa \frac{kT}{h} e^{-\frac{\Delta^* U_V - T\Delta^* S_V}{RT}} = \kappa \frac{kT}{h} e^{-\frac{\Delta^* X_P - T\Delta^* S_P}{RT}} \quad (22)$$

The rate constant $\kappa^\times$ is on the other hand expressed as that

$$\kappa^\times = \kappa \frac{kT}{h} e^{-\frac{\Delta^* F_{V,1}}{RT}} = \kappa \frac{kT}{h} e^{-\frac{\Delta^* U_{V,1} - T\Delta^* S_{V,1}}{RT}} = \kappa \frac{kT}{h} e^{-\frac{\Delta^* X_{P,1} - T\Delta^* S_{P,1}}{RT}} \quad (23)$$

where

$$\bar{F}_{V,1}^{\circ} = \bar{Z}_{P,1}^{\circ} = -RT \log Q^{\circ} = \mu^{\circ} - RT \log N^{\circ} \quad (24F)$$

$$\bar{S}_{V,1}^{\circ} = R \log Q^{\circ} + RT \left(\frac{\partial \log Q^{\circ}}{\partial T} \right)_V = \bar{S}_V^{\circ} + RT \log N^{\circ} \quad (24S_V)$$

$$\bar{U}_{V,1}^{\circ} = \bar{F}_{V,1}^{\circ} + T\bar{S}_{V,1}^{\circ} = \bar{U}_V^{\circ} \quad (24U_V)$$

$$\bar{S}_{P,1}^{\circ} = R \log Q^{\circ} + RT \left(\frac{\partial \log Q^{\circ}}{\partial T} \right)_P - RT\alpha = \bar{S}_P^{\circ} + RT \log N^{\circ} \quad (24S_P)$$

$$\bar{X}_{P,1}^{\circ} = \bar{Z}_{P,1}^{\circ} + T\bar{S}_{P,1}^{\circ} = \bar{X}_P^{\circ} \quad (24X_P)$$

where $\alpha = \left(\frac{\partial \log V}{\partial T} \right)_P$ is the expansion coefficient. A solution is called here ideal when $\bar{F}_{V,1}^{\circ}$ etc. remain constant at constant temperature and pressure independent of variable concentrations. The $\bar{F}_{V,1}^{\circ}$ etc. are however defined here as the properties of any solution

(8) Fowler; Trans. Faraday Soc., **34** (1938), 75, 124.

Guggenheim & Weiss; Trans. Faraday Soc., **34** (1938), 57.

(9) Nernst; "Theoretische Chemie" Thermochemie IV, 4 Kapitel.

(10) Rabinowitch; Trans. Faraday Soc. **34** (1938), 113.

(11) Christiansen; Z. physik. Chem. B **33** (1936), 145; J. Chem. Phys. **7** (1939), 653.

(12) Norish; Trans. Faraday Soc. **34** (1938), 73.

rather than as those of an ideal solution of unit δ concentration. In the case of a perfect gas assembly Q^δ and in consequence $\bar{F}_{T,1}^\delta$, $\bar{S}_{V,1}^\delta$, $\bar{U}_{V,1}^\delta$, $\bar{F}_{P,1}^\delta$, $\bar{S}_{P,1}^\delta$ and $\bar{X}_{P,1}^\delta$ remains constant at constant temperature independent even of pressure.

The temperature variation of v and $k^\times$ are expressed according to Eqs. (21), (22), (23), (24), (14) and (15) as that,

$$RT^2 \left(\frac{\partial \log v}{\partial T} \right)_V = RT + \Delta^* U_V, \quad (25 V)$$

$$RT^2 \left(\frac{\partial \log v}{\partial T} \right)_P = RT + \Delta^* X_P \quad (25 P)$$

$$RT^2 \left(\frac{\partial \log k^\times}{\partial T} \right)_V = RT + \Delta^* U_V \quad (26 V)$$

$$\begin{aligned} RT^2 \left(\frac{\partial \log k^\times}{\partial T} \right)_P &= RT + \Delta^* X_P - RT^2 \alpha \Delta^* \nu \\ &= RT + \Delta^* U_P + P \Delta^* V_P - RT^2 \alpha \Delta^* \nu \end{aligned} \quad (26 P)$$

where $\Delta^* \nu = 1 - \sum \nu_i$ or the critical increment of the number of systems in the assembly.

We have from Eqs. (26), (21), (14), (15) and (16), that,

$$RT^2 \left(\frac{\partial \log k^\times}{\partial T} \right)_P - RT^2 \left(\frac{\partial \log k^\times}{\partial T} \right)_V = T \frac{\alpha}{\beta} \Delta^* V_P - RT^2 \alpha \Delta^* \nu \quad (27)$$

where $\beta = - \left(\frac{\partial \log V}{\partial P} \right)_T$ is the compressibility. Assuming $T = 300^\circ K$, $\Delta^* V_P = 100 \text{ cc}$, $\alpha = 10^{-3} \text{ deg}^{-1}$, $\beta = 10^{-4} \text{ atm}^{-1}$ and $\Delta^* \nu = -1$ (bimolecular) we have 7 kcal for the difference "activation energy" at constant pressure $RT^2 \left(\frac{\partial \log k^\times}{\partial T} \right)_P$ and that at constant volume.

In the case of perfect gas assembly when $\alpha = \frac{1}{T}$, $\beta = \frac{1}{P}$ and $\bar{V}_P^\delta = \frac{RT}{P}$ or $\Delta^* V_P = \frac{RT}{P} \Delta^* \nu$ the above difference exactly vanishes.

(iv) On the basis of the above thermodynamical presentation the controversis among Moelwyn-Hughes,⁽¹³⁾ Evans and Polanyi⁽¹⁴⁾ and Guggenheim⁽¹⁵⁾⁽¹⁶⁾ are commented as follows. Assuming that

$$k^\times = \text{const } e^{-\frac{\Delta^* Q}{kT}} = \text{const } e^{-\frac{\Delta^* E + P \Delta^* V - T \Delta^* S}{kT}}$$

Moelwyn-Hughes derives that,

(13) Moelwyn-Hughes; Trans. Faraday Soc. **32** (1936), 1723.

(14) Evans & Polanyi; Trans. Faraday Soc. **33** (1937), 448.

(15) Guggenheim; Trans. Faraday Soc. **33** (1937), 607.

(16) Guggenheim; Trans. Faraday Soc. **32** (1936), 1333.

$$E_a \equiv RT^2 \frac{d \log k^\times}{dT} = \Delta^* E + P \Delta^* V \left\{ 1 - T \left(\frac{\partial \log \Delta^* V}{\partial T} \right)_P - T \left(\frac{\partial \log P}{\partial T} \right)_V \right\}$$

where $\Delta^* \varphi$, $\Delta^* E$ and $\Delta^* V$ are, as he states, respective critical increments of F , U and V . Evans and Polanyi⁽¹⁴⁾ states that the differentiation is erroneous and correctly performing it the third term in the parenthesis vanishes in agreement with their expression giving the dependence of the activation energy E_a on hydrostatical pressure.

Exact content of Moelwyn-Hughes' $\Delta^* \varphi$ and other quantities with proper associated conditions which fits his statement is deduced to be that,

$$\Delta^* \varphi \equiv \Delta^* F_{T,P}, \quad \Delta^* E \equiv \Delta^* U_P, \quad \Delta^* V \equiv \Delta^* V_P, \quad \Delta^* S \equiv \Delta^* S_P$$

This gives on differentiation of $\log k^\times$, similarly as in case of Eqs. (26), that,

$$\left(\frac{\partial \log k^\times}{\partial T} \right)_V = \Delta^* U_V, \quad \left(\frac{\partial \log k^\times}{\partial T} \right)_P = \Delta^* E + P \Delta^* V - RT^2 \alpha \Delta^* \nu \quad (28 V), (28 P)$$

i.e. even the second term in the parenthesis vanishes. The latter term creeps into the result if $\left[\frac{\partial}{\partial T} \left(\frac{\Delta^* U_P}{RT} - \frac{T \Delta^* S_P}{RT} \right) \right]$ is erroneously identified with $\frac{\Delta^* U_P}{RT^2}$ in analogy to $\left[\frac{\partial}{\partial T} \left(\frac{U - TS}{RT} \right) \right]_V$ which gives exactly $\frac{U}{RT^2}$.

Guggenheim arrives correctly at the special form of Eq. (28 P) valid when $\Delta^* \nu = -1$ (15), without explicitly regard in the distinction between constant volume and pressure. His claim that $k^\times$ ought to be differentiated at constant pressure and his objection against Evans and Polanyi's reason way they do so are however without ground.

We may if preferred differentiate $\log k^\times$ at constant volume as exactly as at constant pressure arriving at even simple r formula (28 V).

(v) Eq. (17 a) may be transformed into a suitable form for discussing the heterogeneous elementary reaction as that,

$$\vec{v}_1 = \frac{\vec{v}}{A} = \kappa \frac{kT}{h} Z_1 \frac{q_{\sigma^*}^{\delta^*}}{p^{\delta^*}} \Theta_{\sigma^*(0)} = \kappa \frac{kT}{h} Z_1 \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^*}^{\delta^M}} \frac{p^{\delta^M}}{p^{\delta^I}} \Theta_{\sigma^*(\delta^M)} \quad (28)$$

where A is the area of the boundary surface, $\vec{v}_1$ the rate per unit area, Z_1 number of σ^* , which holds δ^* per unit area and δ^M the system which occupies σ^* or the catalytic poison. It is deduced from the expression that (a) if $\Theta_{\sigma^*(0)} = 1$ or the boundary surface is nearly clear and $\delta^I = \sum_i \nu_i^I \delta_i^I$ is the system in a perfect gas or in an ideal solution, the rate is proportional to $\prod (N \delta_i^I)^{\nu_i^I}$ according to Eq. (3b), (b) if $\Theta_{\sigma^*(\delta^M)} = 1$ and both δ^I and $\delta^M = \sum_m \nu_m^M \delta_m^M$ are systems in a perfect gas or in an ideal solution the rate is proportional to $\prod (N \delta_i^I)^{\nu_i^I} / \prod (N \delta_m^M)^{\nu_m^M}$ (c) if in the latter case $\delta^I \equiv \delta^M$ the rate is

independent of the concentrations and (d) if δ_i^I 's and δ_m^M 's are partially identical in the similar case, (b) holds true with the remaining part of them. These conclusions are correctly arrived at by Laidler, Glasstone and Eyring⁽¹⁷⁾ extending their theory to the heterogeneous reaction treating the matter analogously to a homogeneous elementary reaction between sites and system.

(v) The temperature variation of the heterogeneous rate is derived from Eq. (28) as that,

$$RT^2 \frac{\partial \log \vec{r}_1}{\partial T} = RT + \Delta^* U_{\sigma^*} + \Delta_{\theta, \sigma^*(0)} U = RT + \Delta^* U_{\sigma^*} - \Delta^M U_{\sigma^*} + \Delta_{\theta, \sigma^*(\delta^M)} U$$

where $\Delta^* U_{\sigma^*} = RT^2 \frac{\partial \log q_{\sigma^*}^{\delta^*}}{\partial T} - RT^2 \frac{\partial \log p^{\delta^I}}{\partial T}$, $\Delta^M U_{\sigma^*} = RT^2 \frac{\partial \log q_{\sigma^*}^{\delta^M}}{\partial T} - RT^2 \frac{\partial \log p^{\delta^M}}{\partial T}$

$$\Delta_{\theta, \sigma^*(0)} U = RT^2 \frac{\partial \log \Theta_{\sigma^*(0)}}{\partial T}, \quad \Delta_{\theta, \sigma^*(\delta^M)} U = RT^2 \frac{\partial \log \Theta_{\sigma^*(\delta^M)}}{\partial T}$$

$\Delta^* U_{\sigma^*}$ or $\Delta^M U_{\sigma^*}$ is according to (V) the increment of U due to withdrawing first δ^I or δ^M from the assembly and then bringing it into σ^* to form δ^* or δ^M there and $\Delta_{\theta, \sigma^*(0)} U$ or $\Delta_{\theta, \sigma^*(\delta^M)} U$ the increment due to evacuating or filling up σ^* with δ^* . It is deduced from the expression that (a) if $\Theta_{\sigma^*(0)} = 1$ or $\Theta_{\sigma^*(\delta^M)} = 1$, $\Delta_{\theta, \sigma^*(0)} U$ or $\Delta_{\theta, \sigma^*(\delta^M)} U$ respectively vanishes so that $RT^2 \frac{\partial \log \vec{r}_1}{\partial T}$ equals $\Delta^* U_{\sigma^*}$ or $\Delta^* U_{\sigma^*} - \Delta^M U_{\sigma^*}$ respectively aside from the minor term RT and that (b) provided that both $\Delta^* U_{\sigma^*}$ and $\Delta^M U_{\sigma^*}$ are nearly constant, the case $\Theta_{\sigma^*(\delta^M)} \approx 1$ is realized only when $\Delta^M U_{\sigma^*} < 0$ and at the lower extremity of temperature where $\log \vec{v}$ increases linearly with $1/T$ with the inclination $\Delta^* U_{\sigma^*} - \Delta^M U_{\sigma^*}$; the inclination gradually decreases as temperature rises until $\log \vec{v}$ increases linearly again with the inclination $\Delta^* U_{\sigma^*}$ at the higher extremity of temperature where $\Theta_{\sigma^*(0)} = 1$.

Admitting that $k^* = \frac{\vec{v}}{H(N_i^I)^{1/2}}$ as defined for the heterogeneous elementary reaction

is proportional to v , (a) is identical with the conclusion arrived at by Hinshelwood⁽¹⁸⁾ apart from the adsorbed state of δ^I assumed by him, which may even be fictitious.

(vi) The rate expression allowed for the mutual interaction between adsorbed systems is exemplified with the catalytic atomization of hydrogen on a metallic catalyst assuming that each metal atom alloyed on a plane square pattern affords a site for an adsorbed hydrogen atom $H(a)$ whereas each adjacent pair of the sites forms a σ^* and the interaction is signifi-

(17) Laidler, Glasstone & Eyring; J. Chem. Phys. **8** (1940), 659, 667.

(18) Hinshelwood; "Kinetics of Chemical Change in Gaseous System" Oxford, (1933), 354.

cant only between directly neighbouring atoms.

$q_{\sigma^*}^{\delta^*} \theta_{\sigma^*(0)}$ in Eq. (28) is expressed according to Eq. (1) as that,

$$q_{\sigma^*}^{\delta^*} \theta_{\sigma^*(0)} = \frac{\Omega C_{\sigma^*(\delta^*)}^{\delta^*}}{\Omega C_0} \quad (29)$$

The above fraction is developed with reference to a group of cites, Σ , consisting of two cites for a particular σ^* and of six directly neighbouring ones which being numbered as shown in the figure. Denoting the partition function of the assembly with Σ clear by $\Omega C_{\Sigma(0)}$ we have similarly as in the case of (5) that,

$$\begin{array}{cccc} & -6 & & \\ -7 & -1 & -5 & \\ -8 & -2 & -4 & \\ & -3 & & \end{array} \quad \Omega C_{\sigma^*(\delta^*)}^{\delta^*} = \Omega C_{\Sigma(0)} q_{\sigma^*,0}^{\delta^*} \sum_{i_3, \dots, i_6} \left(\frac{q_{\sigma^*,0}^{H(a)}}{p^H} \xi^* \right)^{\sum_{i=3}^6 i} \eta_3^{i_3+0.6} \eta_4^{i_4+0.5+0.6+0.7} \eta_5^{i_5+0.4+0.5+0.6+0.7} \eta_6^{i_6+0.4+0.5} \quad (30)$$

$$\Omega C_0 = \Omega C_{\Sigma(0)} \sum_{i_1, \dots, i_6} \left(\frac{q_{\sigma^*,0}^H}{p^H} \right)^{\sum_{i=1}^6 i} \eta_3^{i_3+0.6} \eta_4^{i_4+0.5+0.7+0.8} \eta_5^{i_5+0.4+0.5+0.6+0.7} \eta_6^{i_6+0.4+0.5+0.6+0.7} \quad (31)$$

where θ_1 is 0 or 1 according as the cite is vacant or occupied, ξ^* the Boltzmann factor of the additional work for $H(a)$ due to δ^* situated in the σ^* and ξ that due to an adjacent $H(a)$. Putting in the above expression of ΩC_0 , alternatively $\theta_1=0$, $\theta_3=0$ or $\theta_4=0$ we have respectively $\Omega C_{\sigma_1(0)}$, $\Omega C_{\sigma_3(0)}$ or $\Omega C_{\sigma_4(0)}$, which are to be equated with each other as in the case of (5), i.e.

$$\Omega C_{\sigma_1(0)} = \Omega C_{\sigma_3(0)} = \Omega C_{\sigma_4(0)} \quad (32)$$

on the other hand we have.

$$1 - \theta = \frac{\Omega C_{\sigma(0)}}{\Omega C_0} \quad (33)$$

Estimating $q_{\sigma^*,0}^{\delta^*}$, $q_{\sigma^*,0}^H$, ξ^* and ξ properly and eliminating p^H , η_3 , η_4 , $\Omega C_{\sigma^*(\delta^*)}^{\delta^*}$, ΩC_0 and $q_{\sigma^*}^{\delta^*} \theta_{\sigma^*(0)}$ from Eqs. (28) to (33), we obtain an expression for $\vec{v}$ as a function of θ and temperature.