



Title	41. Stoichiometric Number and Universal Kinetic Law in the Neighbourhood of Equilibrium. (From the Proceedings of the Japan Academy, Vol. 29 (1953), No. 4)
Author(s)	HORIUTI, Juro; ENOMOTO, Saburo
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 3(1)
Issue Date	1953-11
Doc URL	http://hdl.handle.net/2115/24626
Type	bulletin (article)
File Information	3(1)_tenki2.pdf



[Instructions for use](#)

41. Stoichiometric Number and Universal Kinetic Law in the Neighbourhood of Equilibrium. II

By Juro HORIUTI and Saburo ENOMOTO

Research Institute for Catalysis, Hokkaido University, Sapporo

(Comm. by M. KATAYAMA, M.J.A., April 13, 1953)

Conclusions arrived at in the foregoing paper¹⁾ with the system specified there will further be developed with its particular case i) and ii) below. Notations there will be used without further comment and equations there referred to attaching I to their numbers.

Case i) *Reaction (I. 4. δ) may either be homogeneous or heterogeneous, but δ_i^L etc. involved exist practically exclusively in a single phase A, where their activities $a^{\delta_i^L}$ etc. are respectively proportional to their concentrations $N^{\delta_i^L}$ etc., i.e.,*

$$a^{\delta_i^L} \propto N^{\delta_i^L} = n^{\delta_i^L} / V_A, \quad a^{\delta_r^R} \propto N^{\delta_r^R} = n^{\delta_r^R} / V_A \quad (1. L), (1. R)$$

where V_A is the total volume of A.

Eq. (I. 9. \mathfrak{R}) appears now,

$$\vec{\mathfrak{R}} / \overleftarrow{\mathfrak{R}} = C \left\{ \prod_i (N^{\delta_i^L})^{\nu_i^L} / \prod_r (N^{\delta_r^R})^{\nu_r^R} \right\}^{1/\nu(\gamma)} \quad (2)$$

where C is a constant. At equilibrium when $\vec{\mathfrak{R}} = \overleftarrow{\mathfrak{R}}$ we have

$$C^{\nu(\gamma)} = K_N = \prod_r (N_e^{\delta_r^R})^{\nu_r^R} / \prod_i (N_e^{\delta_i^L})^{\nu_i^L}, \quad (3)$$

and hence,

$$\vec{\mathfrak{R}} / \overleftarrow{\mathfrak{R}} = \left\{ K_N \prod_i (N^{\delta_i^L})^{\nu_i^L} / \prod_r (N^{\delta_r^R})^{\nu_r^R} \right\}^{1/\nu(\gamma)} \quad (4)$$

where K_N is the equilibrium constant.

Eq. (I. 11. \mathfrak{R}) on the other hand assumes according to (I. 7), (1. L) and (1. R) the form

$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(\gamma)} \left\{ \sum_i \frac{(\nu_i^L)^2}{n_e^{\delta_i^L}} + \sum_r \frac{(\nu_r^R)^2}{n_e^{\delta_r^R}} + (\sum_i \nu_i^L - \sum_r \nu_r^R) \left(\frac{d \log V_A}{dm} \right)_e \right\} \quad (5)$$

or in particular,

$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(\gamma)} \left\{ \sum_i \frac{(\nu_i^L)^2}{n_e^{\delta_i^L}} + \sum_r \frac{(\nu_r^R)^2}{n_e^{\delta_r^R}} \right\} \quad (6. V)$$

at constant volume V_A , and

$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(\gamma)} \left\{ \sum_i \frac{(\nu_i^L)^2}{n_e^{\delta_i^L}} + \sum_r \frac{(\nu_r^R)^2}{n_e^{\delta_r^R}} - (\sum_i \nu_i^L - \sum_r \nu_r^R) (\sum_i \nu_i^L \bar{V}_P^{\delta_i^L} - \sum_r \nu_r^R \bar{V}_P^{\delta_r^R}) / V_A \right\} \quad (6. P)$$

at constant pressure P of A, where $\bar{V}_P^{\delta_i^L}$ etc. are partial molar volumes of δ_i^L etc. in A respectively. Eqs. (6. V) and (6. P) are coincident with each other, if $\sum_i \nu_i^L = \sum_r \nu_r^R$, i.e., when the reaction involves no alteration

in number of molecules.

In the further special case of the ideal gas mixture of A , when $\bar{V}_P^{\delta_i'}$ etc. all equal RT/P , (6. V) remains invariant, whereas (6. P) assumes the particular form

$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(r)} \left\{ \sum_i \frac{(\nu_i^I)^2}{n_e^{\delta_i^I}} + \sum_r \frac{(\nu_r^K)^2}{n_e^{\delta_r^K}} - (\sum_i \nu_i^I - \sum_r \nu_r^K)^2 / n_e \right\}$$

where $n_e = PV_A/RT$ is the total number of mols in A at equilibrium, which needs not to equal $\sum_i n_e^{\delta_i^I} + \sum_r n_e^{\delta_r^K}$.

We might remark a few points below on the basis of the above development.

A) The present authors determined $\nu(r)$ of the ammonia synthesis reaction²⁾ using the equation

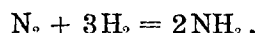
$$r = \frac{2\vec{r}_e}{\nu(r)x_e} (x_e - x) \quad (7)$$

where r or \vec{r}_e was the overall or one-direction rate at equilibrium respectively of ammonia formation and x or x_e the ammonia partial pressure or that at equilibrium respectively. The above equation was derived from (I. 3. V) by a special consideration neglecting the partial pressure variation of hydrogen and nitrogen on account of their huge excess over ammonia.

The kinetic law in the neighbourhood of equilibrium allowed for the variation at constant volume is now given by (I. 12. D) incorporated with (6. V) written in the particular form

$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(r)} \left(\frac{1}{n_e^2} + \frac{9}{n_e^{\text{H}_2}} + \frac{4}{n_e^{\text{NH}_3}} \right) \quad (8)$$

with respect to the chemical equation



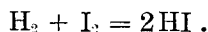
The special case (7) is readily obtained from (8) and (I. 11. m) observing the relations, $2V_s = r$, $2\vec{\mathfrak{R}}_e = \vec{r}_e$ and $2(m - m_e)/n_e^{\text{NH}_3} = (x - x_e)/x_e$ which follow from (I. 7), (I. 12. V) and (I. 6).

B) The relation between the equilibrium constant and the one-direction rate has recently been discussed by a number of authors³⁾⁴⁾⁵⁾⁶⁾. Manes, Hofer, and Weller⁵⁾ have discussed the relation advanced by Gadsby, Hinshelwood, and Sykes³⁾ attributing it to an implicit assumption and put forward an alternative, which is of the same form to (4), as an assumption sufficiently fulfilling the thermodynamic requirement that $\vec{\mathfrak{R}}_e = \vec{\mathfrak{R}}_e$ at equilibrium. The exponent z as they write in place of $1/\nu(r)$ is a positive quantity expected, according to them, to be a small integer or its reciprocal, provided that the relevant chemical equation is written with least integral coefficients.

The exponent acquires now a clear meaning of the reciprocal stoichiometric number. Its value $1/\nu(r)$ is, so far observed, $1^{7) 8)}$ for the hydrogen electrode process on platinum and $1/2$ for the catalyzed ammonia synthesis²⁾ as they expect but it must be in general a positive rational number, possibly very great according to the foregoing paper¹⁾.

It is to be noted that $\nu(r)$ or z needs not to be a constant throughout but may vary as the rate-determining step switches from one elementary reaction over to the other along with the variation of condition.

C) The present conclusion provides a requirement to the rate expression in terms of the rate constant that the value of $\bar{\mathfrak{K}}_e$ appropriate to the expression and $\nu(r)$ to the mechanism underlying to it should conform with observed $[\mathfrak{R}]$ according to (6. V) or (6. P). We might investigate in this regard the classical result of Bodenstein⁸⁾ on the reaction



His observation both of synthesis and decomposition gives, as analysed similarly to that of ammonia reaction²⁾, the following most probable values^{***)}: $[\mathfrak{R}] = (2.67 \pm 0.30) \times 10^{-3} \text{ min.}^{-1}$, $N_e^{\text{H}_2} = N_e^{\text{I}_2} = (4.99 \pm 0.06) \times 10^{-3} \text{ mol./lit.}$ and $N_e^{\text{HI}} = (35.27 \pm 0.06) \times 10^{-3} \text{ mol./lit.}$ at 448°C. ^{***)} Bodenstein's value of the bimolecular rate constant gives on the other hand $\bar{\mathfrak{K}}_e$ value $(6.38 \pm 0.63) \times 10^{-6} \text{ mol. lit.}^{-1} \text{ min.}^{-1}$ and hence $\nu(r) = 1.3 \pm 0.2$ according to (6. V). This agrees almost within the experimental error with $\nu(r) = 1$ implied in his bimolecular mechanism.

Case ii) *The system consists of a phase A and a sorbent S. The reaction, $\delta^L = \delta^R$ of (I. 4. δ) is here the conversion of $\delta(A)$ consisting in a single molecule in A having activity proportional to its concentration, into $\delta(S)$ in or on S, which may be dissociated or not.*

^{*)} This value is $1/2$ instead according to Frumkin [Disc. Faraday Soc. "Electrode Process", 1947, 57].

^{***)} Eq. (I. 12. I) was written in the form,

$$\log(N_e^{\text{HI}} - N^{\text{HI}}) = -[\mathfrak{R}]t + a$$

$$\log(N^{\text{HI}} - N_e^{\text{HI}}) = -[\mathfrak{R}]t + b$$

for synthesis and decomposition respectively where a and b are constants. The N_e^{HI} was now adjusted to $N_e^{\text{HI}'}$ which gives common $[\mathfrak{R}]$ value from data both of the cases. The above equations was then written in the linear form by expansion with respect to $\Delta N^{\text{HI}} = N_e^{\text{HI}} - N_e^{\text{HI}'}$ as,

$$\log(N_e^{\text{HI}'} - N^{\text{HI}}) + \frac{\Delta N^{\text{HI}}}{N_e^{\text{HI}'} - N^{\text{HI}}} = -[\mathfrak{R}]t + a, \quad \log(N^{\text{HI}} - N_e^{\text{HI}'}) + \frac{\Delta N^{\text{HI}}}{N^{\text{HI}} - N_e^{\text{HI}'}} = -[\mathfrak{R}]t + b$$

and ΔN^{HI} and $[\mathfrak{R}]$ were now determined by the method of least square with synthesis and decomposition data simultaneously using the above two as the observation equations. The most probable value of N_e^{HI} was taken as $N_e^{\text{HI}'} + \Delta N^{\text{HI}}$.

^{***)} Bodenstein's N_e^{HI} value determined by a separate experiment gives according to (I. 12. I) rather diverging values of $[\mathfrak{R}]$ for synthesis and decomposition, *i.e.*, $(2.7 \pm 0.5) \times 10^{-3} \text{ min.}$ and $(2.0 \pm 0.2) \times 10^{-3} \text{ min.}^{-1}$ respectively.

Eqs. (I. 4. δ), (I. 7) and (I. 11. \mathfrak{R}) are now in this particular case respectively

$$\delta(A) = \delta(S)$$

$$m - m_e = n_e^{\delta(A)} - n_e^{\delta(A)} = n_e^{\delta(S)} - n_e^{\delta(S)} \quad (9. m)$$

and
$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(r)} \left\{ \left(\frac{d \log a^{\delta(S)}}{dm} \right)_e - \left(\frac{d \log a^{\delta(A)}}{dm} \right)_e \right\}, \quad (9. \mathfrak{R})$$

m being here sorbed quantity itself. The activity $a^{\delta(S)}$ in the above equation may be replaced by the activity $a_m^{\delta(A)}$ of $\delta(A)$ supposed to be at equilibrium with $\delta(S)$ at momentary m , which equals $a^{\delta(S)}$ according to (I. 8), and $\left(\frac{d \log a_m^{\delta(A)}}{dm} \right)_e$ in turn by $\left(\frac{d \log N_m^{\delta(A)}}{dm} \right)_e$ according to the assumed proportionality, $N_m^{\delta(A)}$ being $N^{\delta(A)}$ appropriate to $a_m^{\delta(A)}$. We have hence,

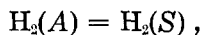
$$\left(\frac{d \log a^{\delta(S)}}{dm} \right)_e = \left(\frac{d \log N_m^{\delta(A)}}{dm} \right)_e,$$

suffix e denoting the actual equilibrium at m_e particular to the given condition of the system. Rewriting $\left(\frac{d \log a^{\delta(A)}}{dm} \right)_e$ further into $\left(\frac{d \log N_m^{\delta(A)}}{dm} \right)_e$ according to the proportionality, we have from (9. \mathfrak{R}),

$$[\mathfrak{R}] = \frac{\vec{\mathfrak{R}}_e}{\nu(r)} \left\{ \left(\frac{d \log N_m^{\delta(A)}}{dm} \right)_e - \left(\frac{d \log N_m^{\delta(A)}}{dm} \right)_e \right\}. \quad (10)$$

The first term in the parenthesis $\{ \}$ is derivable from the observed sorption isotherm, whereas the second one depends on the condition of the system: It vanishes of course at constant $N^{\delta(A)}$ which is realized at infinite magnitude of A or more practically in the case of a proper flow of A of constant composition over S or of pure phase A of $\delta(A)$ kept at constant pressure.

The $\nu(r)$ worked out according to (10) from observations of $[\mathfrak{R}]$ and $\vec{\mathfrak{R}}_e$ affords a criterion for the sorption mechanism. If for instance two atoms of hydrogen molecule are statistically independent or dependent on each other at the critical state of the rate-determining step, thus occurring twice or once respectively for every completion of the sorption reaction



$\nu(r)$ is 2 or 1 respectively.

Eq. (10) provides alternatively the experimental value of $\vec{\mathfrak{R}}_e/\nu(r)$ to be compared with theoretical one derived from any assumed mechanism of sorption.

Present authors wish to express their sincere thanks to Prof. M. Katayama for his kind interest and valuable advices on the foregoing two papers.

References

- 1) J. Horiuti : Proc. Japan Acad., **29**, 160 (1953).
- 2) S. Enomoto and J. Horiuti : Proc. Japan Acad., **28**, 493,499 (1952).
- 3) J. Gadsby, C.N. Hinshelwood, and K.W. Sykes : Proc. Roy. Soc. London, **187**, 129 (1946).
- 4) I. Prigogine, P. Outer, and CL. Herbo : J. Phys. Coll. Chem., **52**, 321 (1948).
- 5) M. Manes, L.J.E. Hofer, and S. Weller : J. Chem. Phys., **18**, 1355 (1950).
- 6) C.A. Hollingsworth : J. Chem. Phys., **20**, 921 (1952).
- 7) J. Horiuti and M. Ikusima : Proc. Imp. Acad., **15**, 39 (1939).
- 8) M. Bodenstein : Z. physik. Chem., **13**, 56 (1894).