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# COMMENTS ON HORIUTI'S STOICHIOMETRIC NUMBER CONCEPT

By

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*The stoichiometric number concept*

This paper represents a summary and extension of some of the ideas which Horiuti[1] and his colleagues pioneered. Their researches on the stoichiometric number concept have appeared in many papers in this Journal. Summaries have also appeared elsewhere.[2,3]

In steady state open flow systems involving heterogeneous catalysis rates of individual mechanistic steps will be constant and chemisorbed intermediates will attain constant concentrations corresponding to given ambient pressure, temperature and concentration of reacting species. The rates of these steps are linked to thermodynamics by the following relationship derived from absolute rate theory:

$$\frac{v_{+s}}{v_{-s}} = \exp(-\Delta g_s/RT) \qquad (1)$$

where,

$v_{\pm s}$ = rates of conversion per unit mass of catalyst for forward and reverse mechanistic step $s$.
$-\Delta g_s$ = Gibbs free energy decrease for step $s$.
$T$ = absolute temperature
$R$ = gas constant

For a single overall reaction the energy change is the sum of that for each step multiplied by the stoichiometric number $\nu_s$ of that step:

$$\Delta G = \sum_{s=1}^{s=n} \nu_s \Delta g_s \qquad (2)$$

The stoichiometric number, first employed by Horiuti, is defined as the number of times each step must occur to add up to the overall reaction.

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As a simple example consider a mechanism for the oxidation of sulfur dioxide according to the following scheme:

$$\begin{array}{lll} & & \nu_s \\ SO_2+\ell & \rightleftarrows SO_2\ell & 2 \\ O_2+2\ell & \rightleftarrows 2O\ell & 1 \\ SO_2\ell+O\ell & \rightleftarrows SO_3\ell+\ell & 2 \\ SO_3\ell & \rightleftarrows SO_3+\ell & 2 \\ \hline 2SO_2+O_2 & = 2SO_3 & \end{array} \qquad (3)$$

Here $\ell$ represents surface sites for chemisorption.

Equations (1) and (2) may be combined to obtain the following:

$$\prod_{s=1}^{s=n}\left(\frac{v_{+s}}{v_{-s}}\right)^{\nu_s}=\exp(-\Delta G/RT) \qquad (4)$$

This equation will only be useful when $v_{\pm s}$ assume finite values, so that all steps are reversible. Some may be at equlibrium with $v_{+s}=v_{-s}$. Horiuti showed that in cases where a single rate controlling step exists for a given overall reaction with a single mechanism, the left side of Eq. (4) can be replaced by the overall reaction velocities since the entire free energy change is accounted for by the single step:

$$\left(\frac{V_+}{V_-}\right)^{\nu_r}=\exp(-\Delta G/RT) \qquad (5)$$

where,

$V_+$ = forward overall reaction velocity
$V_-$ = reverse overall reaction velocity
$-\Delta G$ = overall Gibbs free energy decrease
$\nu_r$ = stoichiometric number of the rate controlling step of the mechanism

For an overall reaction expressed in the form;

$$aA+bB+\cdots \rightleftarrows pP+qQ+\cdots \qquad (6)$$

Equation (4) can be expressed in the following convenient form;

$$V=V_+-V_-=V_+\left[1-\left(\frac{p_P^p p_b^q\cdots\cdots}{K_P p_A^a p_B^b\cdots\cdots}\right)^{\frac{1}{\nu_r}}\right] \qquad (7)$$

where,

$V$ = overall reaction velocity
$p$ = partial pressure of terminal species subscripted
$K_p$ = equilibrium constant

If the rate controlling step does not change during the course of a chemical reaction, Equation (7) can be employed for the construction of rate equations. The factor in brackets in Equation (7) is termed the "potential factor". It includes the effect of thermodynamics on reaction rate and approaches zero as equilibrium conversion is reached.

*The potential factor*

Since Equation (7) is very useful in practical applications, it is of interst to establish when it can be applied without the restriction of a single rate controlling step. The conditions for which a potential term can be factored from a rate expression have been discussed by Csuha and Happel.[4] Where more than one rate controlling step exists for a given overall reaction mechanism or "reaction route" the unidirectional velocities $V_{\pm}$ are not always unique but depend on the traced atomic species used in their determination. Unique overall velocities only occur when all slow steps for a reaction are present in a single path for atomic transfer from a reactant to product.

Temkin[5] has also made important contributions to this problem and carried forward some by Horiuti's ideas. As was shown by him the unidirectional velocities in a reaction path can be expressed as follows:

$$\frac{V_+}{V_-} = \prod_{s=1}^{s=n} \frac{v_{+s}}{v_{-s}} \qquad (8)$$

If all steps in that path correspond to the same stoichiometric number, Eqs. (4)-(7) will still apply. However, these equations will not apply if slow steps occur in more than one path of atomic transfer. If slow steps occur in branches of a mechanistic path, it is not possible to uniquely specify $V_{\pm}$ even if these steps all are included in the same mechanism or "reaction route". This point is not clear from Temkin's[5] treatment.

A unique way to determine whether a given reaction can be characterized by a rate equation with a factorable potential expression consists in measuring forward and reverse rates of transfer of atomic species by means of tracers. Some further considerations in applying this procedure to the development of rate equations are discussed by Happel.[6]

*General thermodynamic considerations*

Even when it is not possible to derive a rate expression with a potential term, Eq. (4) will still serve to check the consistency of a set of step velocities obtained by modelling of rate data for a single overall reaction.

In the case of a more complicated system involving more than a single overall reaction occuring simultaneously, the overall system may be viewed

as composed of a set of individual overall reactions each of which is governed by a mechanism which obeys Eq. (4). Where common mechanistic steps occur it may be difficult to separate velocity components for the individual reactions.

In such cases, it is possible to write an expression similar to Eq. (4) as applied to the total free energy decrease for the entire system to arrive at equilibrium. Thus, for any appropriate set of mechanistic steps each step will occur $\phi_s$ times corresponding to a single occurrence for one of the independent overall reactions, which may be arbitrarily chosen as a reference. Then we obtain :

$$\prod_{s=1}^{s=n}\left(\frac{v_{+s}}{v_{-s}}\right)^{\phi_s}=\exp\left(-\Delta G/RT\right) \qquad (9)$$

where $\Delta G$ now refers to the entire system of species.

As an example of the application of Eq. (9) consider the methanation of carbon monoxide. The terminal species to be employed for calculation of $\Delta G$ are $H_2$ CO, $CH_4$, $CO_2$ and $H_2O$. A mechanism might be considered which involves the following two independent reactions :

$$3H_2+CO \rightleftarrows CH_4+H_2O$$

$$2CO+2H_2 \rightleftarrows CH_4+CO_2$$

If the first reaction is taken as a reference, we may designate the rate of production of $CO_2$ by $\alpha$ corresponding to a unit rate of production of $H_2O$ by the first reaction. Some mechanistic steps will involve simple linear functions of $\alpha$ depending on the mechanism chosen. Equation (9) provides an independent means for checking the step velocities predicted from experimental data by a chosen mechanism. When only the first overall reaction is involved $\alpha=0$ and $\phi_r$ in Eq. (9) is replaced by the stoichiometric number $\nu_r$.

Thus for cases where an equilibrium condition is approached, the above relationships show how thermodynamic factors influence the rate processes involved. The development of these ideas also illustrates the seminal nature of Horiuti's contributions to problems in heterogeneous catalysis.

## References

1) J. Horiuti and M. Ikushima, Proc. Imp., Acad. Gap. **15**, 39 (1939).
2) J. Horiuti and T. Nakamura, Adv. in Catal., **17**, 1. (1967).
3) J. Horiuti, Ann. N. Y. Acad. Sci., **213**, 5 (1973).
4) R. S. Chuha and J. Happel, AIChE Journal, **17**, 927 (1971).
5) M. I. Temkin, Adv. in Catal., **28**, 173 (1979).
6) J. Happel, AIChE Journal, **24**, 368 (1978).