JOURNAL OF CATALYSIS 2, 366–370 (1963)

A General Rule in Chemisorption of Gases on Metals

KEN-ICHI TANAKA AND KENZI TAMARU

From the Department of Chemistry, Yokohama National University,
Minami-ku, Yokohama, Japan

Received April 20, 1963

A general rule in chemisorption of gases on metals is proposed. According to the rule, the initial heats of chemisorption of gases such as oxygen, ethylene, nitrogen, hydrogen, and ammonia, on various metal surfaces are empirically expressed by the following equation:

$$Q_0 = a[(-\Delta H_0^\circ) + 37] + 20 \text{ kcal/mole}$$

where Q_0 is the initial heat of chemisorption, a, a constant which depends upon the kind of gas, and $-\Delta H_0^\circ$, the heat of formation of the highest oxide per metal atom. Consequently, if a heat of chemisorption of a gas on a metal is known (or if a is assessed for the gas), all the values of the initial heats of chemisorption of the gas on various metal surfaces can be approximately estimated.

Since Taylor (*1*) emphasized the importance of chemisorption in heterogeneous catalysis, much attention has been focused on the nature of chemisorption of gases on various catalyst surfaces. The behavior of various gases on metal surfaces has been studied with many methods such as, for instance, volumetric, calorimetric, electronic, magnetic, and spectroscopic methods (*2*). The nature of the bond between adsorbed species and metal surface, accordingly, has been envisaged, and has frequently been associated with the electronic structure and crystal parameter of metals (*3*).

Trapnell (*2*) pointed out a marked specificity in the chemisorption of gases on evaporated metal films at temperatures lower than the room temperature. Recently the heat of chemisorption was successfully correlated with the heat of formation of bulk compound by such people as Roberts (*4*), Brennan (*5*), and Sachtler and van Reijen (*6*). Their findings strongly suggest that the chemisorption bond is similar in its nature to that in the bulk compound.

The elucidation of the nature of chemisorption would lead directly to that of heterogeneous catalysis, and a general rule applicable in chemisorption would also apply to heterogeneous catalysis. This would be of great industrial importance.

THE HEAT OF FORMATION OF METAL COMPOUNDS

The stability of metal oxides, or the standard free energy of formation of metal oxides, is plotted against the corresponding

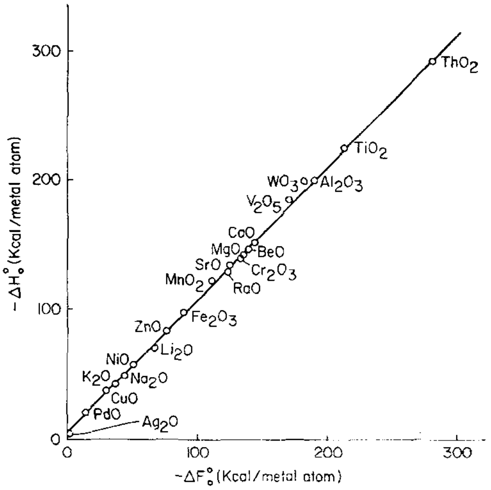

FIG. 1. The standard free energy of formation per metal atom ($-\Delta F_0^\circ$) and the standard heat of formation per metal atom ($-\Delta H_0^\circ$) of oxides.

standard heat of formation as shown in Fig. 1 (*7*), where a satisfactory correlation of the two heats is established.

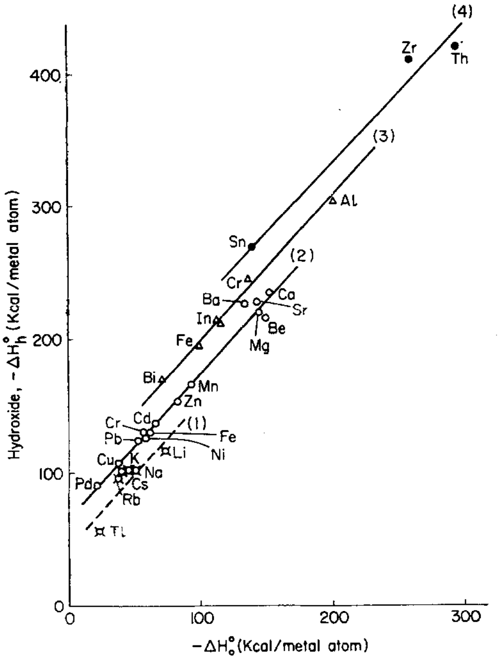

FIG. 2. The standard heat of formation of metal hydroxide per metal atom ($-\Delta H_h^\circ$) and that of the oxide per metal atom ($-\Delta H_o^\circ$). The number of valences is designated in the parentheses.

The heats of formation of metal oxides are plotted against those of hydroxides in Fig. 2, where the following equation is applicable;

$$\mathrm{Me(OH)}_n \rightarrow \mathrm{MeO}_{n/2} + (n/2)\mathrm{H_2O} \qquad (1)$$

$$\Delta H_h^\circ = \Delta H_o^\circ + (n/2)\Delta H_w^\circ + (n/2)Q_d$$

where ΔH_h°, ΔH_o°, and ΔH_w° are the standard heats of formation of hydroxide, oxide, and liquid water, respectively, and Q_d is the heat of dehydration per mole of water. As shown in Fig. 2, Q_d depends upon the valence of the metals rather than the kind of metals.

The heats of formation of many salts such as sulfates, formates, nitrates, oxalates, and so forth are plotted against the heat of formation of the corresponding oxides, which are shown in Figs. 3–5, (*8*). All the figures show a good linearity between them. Consequently the following conclusion can be derived: The heats of formation of metal compounds are in the definite order of metals, being independent of the kind of compounds, and are linear with each other. The slope and the intercept of the straight lines in these correlations are determined by the nature of the electronegative groups with which metals are combined.

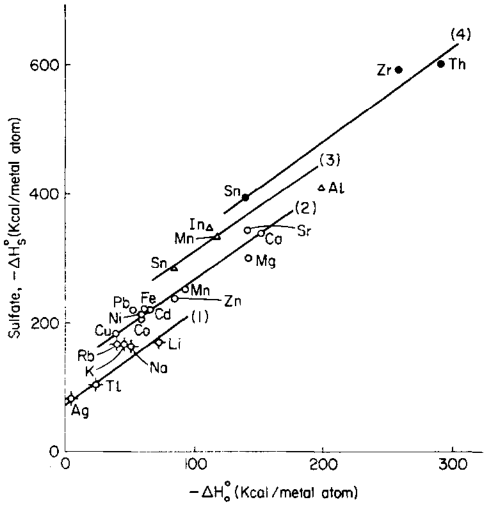

FIG. 3. The standard heat of formation of metal sulfate per metal atom ($-\Delta H_s^\circ$) and that of the oxide per metal atom ($-\Delta H_o^\circ$).

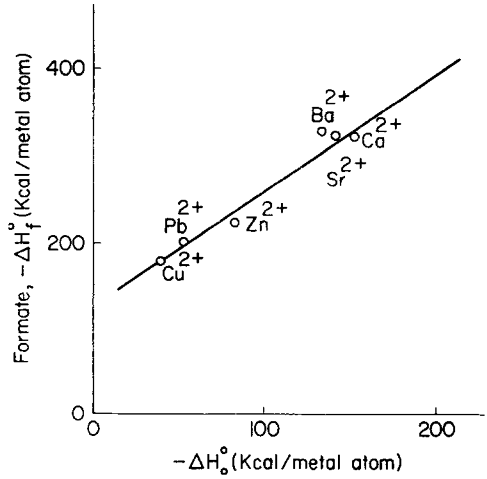

FIG. 4. The standard heat of formation of metal formate per metal atom ($-\Delta H_f^\circ$) and that of the oxide per metal atom ($-\Delta H_o^\circ$).

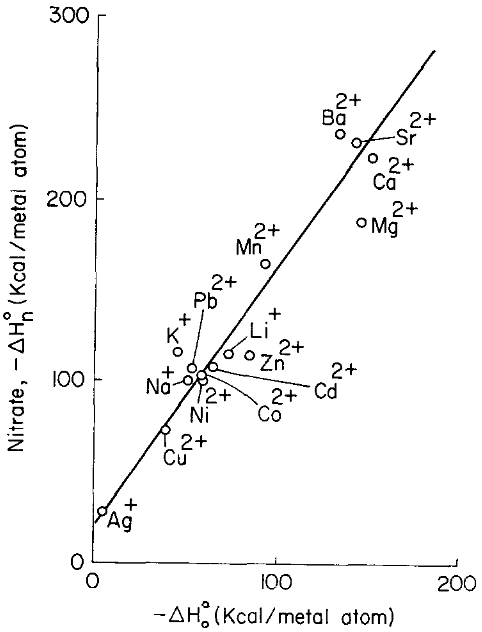

Fig. 5. The standard heat of formation of metal formate per metal atom ($-\Delta H_f^\circ$) and that of the oxide per metal atom ($-\Delta H_o^\circ$).

The Heat of Chemisorption

The heats of chemisorption of gases on metals are to be interpreted as the heats of formation of surface compounds and it is not surprising that they can be correlated with the heats of formation of other bulk metal compounds. Accordingly, the heats of chemisorption of gases on various metals are associated with the heats of formation of metal compounds between the gases and the metals.

One of the specific properties of the solid surface is that the stoichiometry in the chemisorption is different from that in the bulk compound. The former is primarily common to the metals of various valences for a certain gas and a certain number (or fraction) of adsorbed molecule (or atom) is assigned to one surface metal atom. Consequently, the heat of formation of metal compounds per metal atom, instead of per mole of oxide or mole of oxygen, is employed to correlate with the initial heat of chemisorption. This is shown in Fig. 6, where the heats of formation of the highest oxides per metal atom are taken in the abscissa.

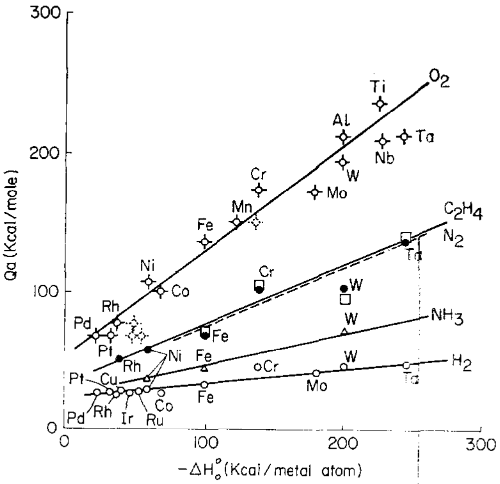

Fig. 6. The correlation between the initial heat of adsorption of various gases (Q_{ads}) and the standard heat of formation of the highest oxide per metal atom ($-\Delta H_o^\circ$).

The initial heats of chemisorption of oxygen (*5*), ethylene (*10*), hydrogen (*11*), nitrogen (*12*), and ammonia (*13*) on various evaporated metal films are correlated with the heats of formation of the highest oxides per metal atom, ($-\Delta H_o^\circ$).*

As shown in Fig. 6, the initial heats of chemisorption of gases on metals are in the definite order of metals and are linear to the heats of formation of the highest oxides per metal atom.

In this way the following general empirical

---

* The "highest" valences of all the metals are taken from the "Handbook of Chemistry" by Lange (*8*) or "Fundamental Chemistry" by Deming (*9*). They are almost all generally accepted values. However, the valences of such metals as Mn, Pd, Ir, Rh, and Pt are rather obscure and are listed as 7, 4, 6, 4, and 6, respectively, while no heats of formation of these "highest" oxides are available in the literature. Accordingly, they are provisionally taken as 4, 2, 4, 3, and 4, respectively, as those are the highest oxides for which the heats of formation are available in the literature. The results are shown in Fig. 6 with solid circles. The heats for the former "highest" oxides, on the other hand, are estimated by extrapolating the heats of formation of lower oxides or from the values of hydroxides, which are plotted in Fig. 6 with dotted circles. No estimation is possible for Ir of 6 valences and, therefore, the value of 4 valences is taken in the figure.

equation is obtained for the initial heats of chemisorption of gases:

$$Q_0 = a\{(-\Delta H^\circ_0) + 37\} + 20$$

If a heat of adsorption of a gas on a metal surface is known (from which a is assessed for the gas), all the values of the initial heats of chemisorption of the gas on metal surfaces can be approximately estimated.

The values of a for oxygen, nitrogen, and hydrogen are correlated with their electronegativity in Fig. 7, where it is shown that the more the gases are electronegative, the higher are the heats of chemisorption.

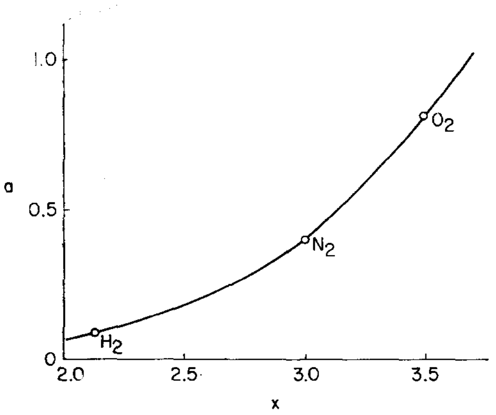

FIG. 7. The values of a for oxygen, nitrogen, and hydrogen are plotted against their electronegativity.

The drop of the heat of chemisorption (Q) of hydrogen with the degree of coverage up to 0.2 (*12*) is approximately proportional to $(-\Delta H^\circ_0)$ as shown in Fig. 8. Thus,

$$Q = Q_0 - \alpha\theta \quad \text{and} \quad \alpha = \alpha_0(-\Delta H^\circ_0)$$

On the basis of these facts it has been shown that $(-\Delta H^\circ_0)$ can be a good empirical parameter to deal with the heats of chemisorption of gases on metal surfaces. The specificity in chemisorption, as was indicated by Trapnell, is accordingly due to the specificity in the rate of chemisorption rather than that in the thermodynamical equilibria of chemisorption. The fact that some of the gases which are not chemisorbed at lower temperatures are chemisorbed at higher temperatures seems to be evidence in support of the view. The behavior of hydrogen on the surfaces of copper (*14*), germanium (*15*), and silver (*16*) is probably an example.

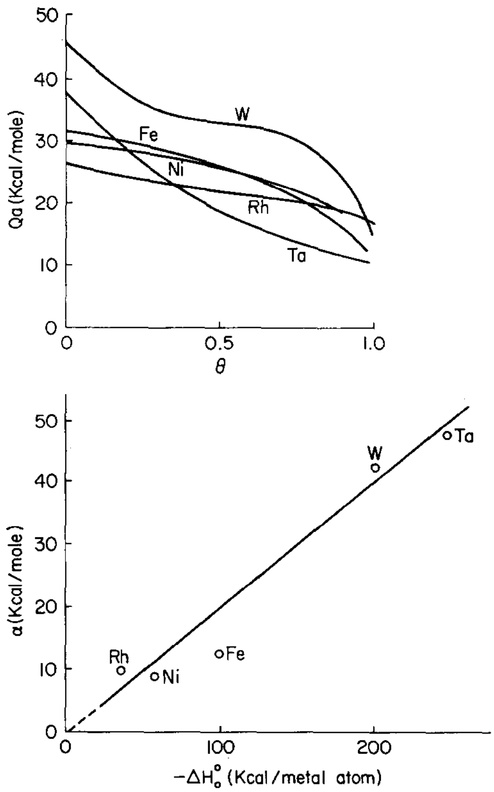

FIG. 8. The drop of the heat of chemisorption of hydrogen with the degree of coverage up to 0.2 is plotted against the standard heat of formation of the highest oxide per metal atom $(-\Delta H^\circ_0)$.

The drop of the heat of adsorption with coverage has been discussed from various viewpoints such as heterogeneity of surface, interaction between adsorbed species, and so forth. But it may reasonably be associated with the concept of induced heterogeneity or work-function effect enunciated by Boudart (*17*) and developed by de Boer and Mignolet (*3*). The heat of adsorption decreases with coverage depending upon the extent of surface dipole formed by the chemisorption, while the difference in electronegativity between the gases and the metal surface determines the extent of the dipole moment as well as the strength of the chemisorption bond.

It is generally accepted that different adsorption states are involved in chemisorption in usual cases (*6*), but as a matter of fact the heat of chemisorption seems to be treated not taking this factor into serious consideration, seemingly because of the similar heat of adsorption.

Generally speaking, heterogeneous catalysis is closely related to chemisorption. The general rule in chemisorption, which is based on the empirical parameter of $(-\Delta H_0^\circ)$, is most probably connected with heterogeneous catalysis on the same basis. Accordingly many data on catalytic kinetics are treated with the empirical parameter. The detailed discussion will be presented in the following paper.

REFERENCES

1. TAYLOR, H. S., *J. Am. Chem. Soc.* **53,** 578 (1931).
2. See e.g. TRAPNELL, B. M. W., *in* "Chemisorption" (W. E. Garner, ed.), Butterworths, London, 1955.
3. See e.g., Dowden. D. A., *in* "Chemisorption" (W. E. Garner, ed.), p. 1 and deBoer, J. H., *ibid.*, p. 27. Butterworths, London, 1957.
4. ROBERTS, M. W., *Nature* **188,** 1020 (1960).
5. BRENNAN, D., HAYWARD, D. O., AND TRAPNELL, B. M. W., *Proc. Roy. Soc.* (*London*) **A256,** 81 (1960).
6. SACHTLER, W. M. H., AND VAN REIJEN, L. L., Shokubai (Tokyo) **4,** 147 (1962).
7. BREWER, L., *Chem. Rev.* **52,** 1 (1953).
8. LANGE, N. A., "Handbook of Chemistry." Handbook Publishers, Inc., Sandusky, Ohio, 1956.
9. DEMING, H. G., "Fundamental Chemistry," 2nd ed. John Wiley, New York.
10. BEECK, O., *Disc. Faraday Soc.* **8,** 118 (1950).
11. STEVENSON, D. P., *J. Chem. Phys.* **23,** 203 (1955).
12. BEECK, O., *Adv. in Catalysis* **2,** 151 (1950); *Disc. Faraday Soc.* **8,** 314 (1950). BAGG, J., AND TOMPKINS, F. C., *Trans. Faraday Soc.* **51,** 1071 (1955).
13. WAHBA, M., AND KEMBALL, C., *Trans. Faraday Soc.* **49,** 1351 (1953).
14. KWAN, T., *Adv. in Catalysis* **6,** 67 (1954).
15. TAMARU, K., *J. Phys. Chem.* **61,** 647 (1957); BENNETT, M. J., AND TOMPKINS, F. C., *Trans. Faraday Soc.* **58,** 816 (1962).
16. MIKOVSKY, R. J., BOUDART, M., AND TAYLOR, H., *J. Am. Chem. Soc.* **76,** 3814 (1954).
17. BOUDART, M., *J. Am. Chem. Soc.* **72,** 3556 (1952).