CORRECTION TO THE PAPER "ISOTHERM OF DISSOCIATIVE ADSORPTION OF HYDROGEN ALLOWED FOR REPULSIVE INTERACTIONS AMONG ADSORBED ATOMS" BY HORIUTI AND HIROTA[1]

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TOYA has pointed out an error involved in the paper[1] mentioned in the title, which is going to be corrected in the present note.

The adsorption isotherm on the (110)-lattice plane of nickel was calculated statistical-mechanically[1], assuming that each lattice point of the plane provided a physically identical adsorption site, allowing for the repulsive interactions among adsorbed hydrogen atoms. The calculation was based on the fundamental equation[1][2]

$$\frac{\theta}{1-\theta} = \frac{q_\sigma^H}{p^H} ,$$

where θ was the covered fraction of the identical sites of adsorption, p^H the BOLTZMANN factor of the chemical potential of hydrogen atom and q_σ^H the BOLTZMANN factor of the free energy increase of the whole system concerned due to addition of a hydrogen atom to a preliminarily evacuated, definite site σ from outside the system; q_σ^H/p^H is hence the BOLTZMANN factor of the free energy increase of the system caused by bringing a hydrogen atom from anywhere within the system onto the preliminarily evacuated, definite site σ.

The free energy increase $-kT \ln q_\sigma^H/p^H$ or the reversible work required was expressed[1] as

$$-kT \ln q_\sigma^H/p^H = w + W/N_A ,$$

where W/N_A was the reversible work due to the repulsive interactions (N_A: the Avogadro's number) between the hydrogen atom brought up to the preliminarily evacuated, definite site σ and those adsorbed on the surrounding sites and w was that required to bring up a hydrogen atom from anywhere in the system

1) J. HORIUTI and K. HIROTA, this volume, p. 51.
2) J. HORIUTI, this Journal, 1, 8 (1948-51).
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onto the σ in the absence of the repulsive interactions mentioned. The above two equations lead to the expression of W, *i.e.*

$$W = RT \ln \frac{1-\theta}{\theta} \cdot \gamma \ ,\tag{1}$$

where

$$\gamma = \exp(-w/kT) \ .$$

The adsorption isotherm was calculated in terms of θ as a function of γ, allowing, particularly in the third approximation, for the repulsive potentials R_{I}, R_{II} and R_{III} respectively between the first, second and third nearest neigh-
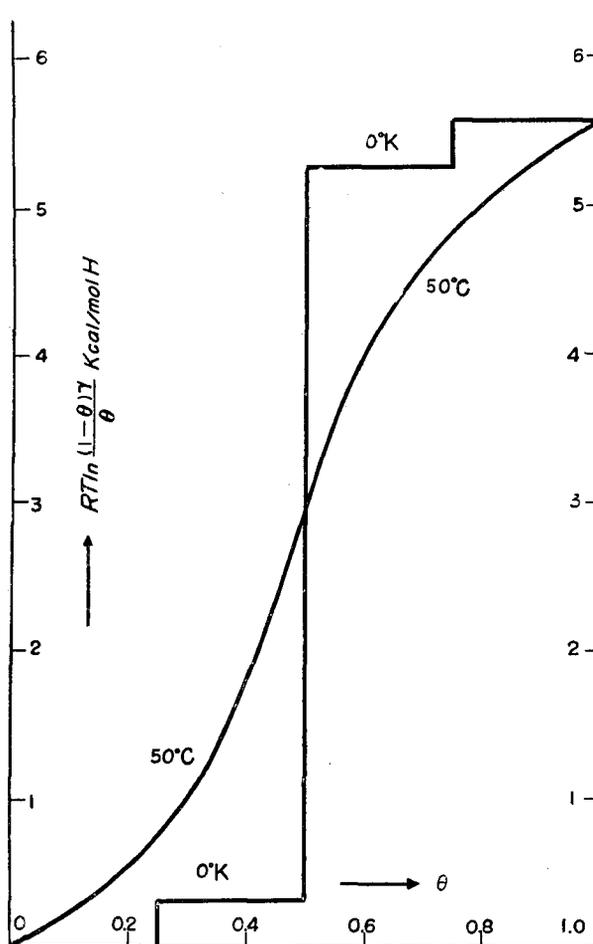

Fig. 1. Free energy of repulsion.

bouring pairs of adsorbed hydrogen atoms. The W at 50°C was calculated by (1) from the result of the third approximation as a function of θ and compared with the tierlike dependence of W on θ reckoned for the absolute zero temperature[1].

The erroneous conclusion in question is now that W at the absolute zero temperature leaps from $4R_{\mathrm{III}}$ to $2R_{\mathrm{I}}+2R_{\mathrm{II}}+4S_{\mathrm{III}}$ at $\theta=1/2$, which keeps constant up to $\theta=1$[1]. The correct conclusion is, as readily seen from the basic model[1], that W leaps, as θ increases, first from 0 to $4R_{\mathrm{III}}$ at $\theta=1/4$, then from $4R_{\mathrm{III}}$ to $2R_{\mathrm{I}}+2R_{\mathrm{II}}$ (instead to $2R_{\mathrm{I}}+2R_{\mathrm{II}}+4R_{\mathrm{III}}$) at $\theta=1/2$ and finally from $2R_{\mathrm{I}}+2R_{\mathrm{II}}$ to $2R_{\mathrm{I}}+2R_{\mathrm{II}}+4R_{\mathrm{III}}$ at $\theta=3/4$, keeping constant over the respective intervals of θ.

In consequence, the last sentence of the first paragraph on p. 70 of the paper[1] should be read "A furthur addition of adsorbed hydrogen atoms causes W to leap to $2R_{\mathrm{I}}+2R_{\mathrm{II}}$ as seen from Fig. 3, which keeps constant until θ attains to 3/4, and then finally to the highest value $2R_{\mathrm{I}}+2R_{\mathrm{II}}+4R_{\mathrm{III}}$, which is maintained from $\theta=3/4$ up to $\theta=1$" and Fig. 4 in the paper[1] replaced by Fig. 1 in this note.