



Title	CORRECTION TO THE PAPER “ ISOTHERM OF DISSOCIATIVE ADSORPTION OF HYDROGEN ALLOWED FOR REPULSIVE INTERACTIONS AMONG ADSORBED ATOMS ” BY HORIUTI AND HIROTA
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**CORRECTION TO THE PAPER "ISOTHERM OF  
DISSOCIATIVE ADSORPTION OF HYDROGEN ALLOWED  
FOR REPULSIVE INTERACTIONS AMONG  
ADSORBED ATOMS" BY HORIUTI AND HIROTA<sup>1)</sup>**

By

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TOYA has pointed out an error involved in the paper<sup>1)</sup> 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<sup>1)</sup>, 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<sup>1)2)</sup>

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

where  $\theta$  was the covered fraction of the identical sites of adsorption,  $p^H$  the BOLTZMANN factor of the chemical potential of hydrogen atom and  $q_{\sigma}^H$  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  $\sigma$  from outside the system;  $q_{\sigma}^H/p^H$  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  $\sigma$ .

The free energy increase  $-kT \ln q_{\sigma}^H/p^H$  or the reversible work required was expressed<sup>1)</sup> as

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

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  $\sigma$  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  $\sigma$  in the absence of the repulsive interactions mentioned. The above two equations lead to the expression of  $W$ , *i. e.*

$$W = RT \ln \frac{1-\theta}{\theta} \gamma, \quad (1)$$

where

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

The adsorption isotherm was calculated in terms of  $\theta$  as a function of  $\gamma$ , 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-

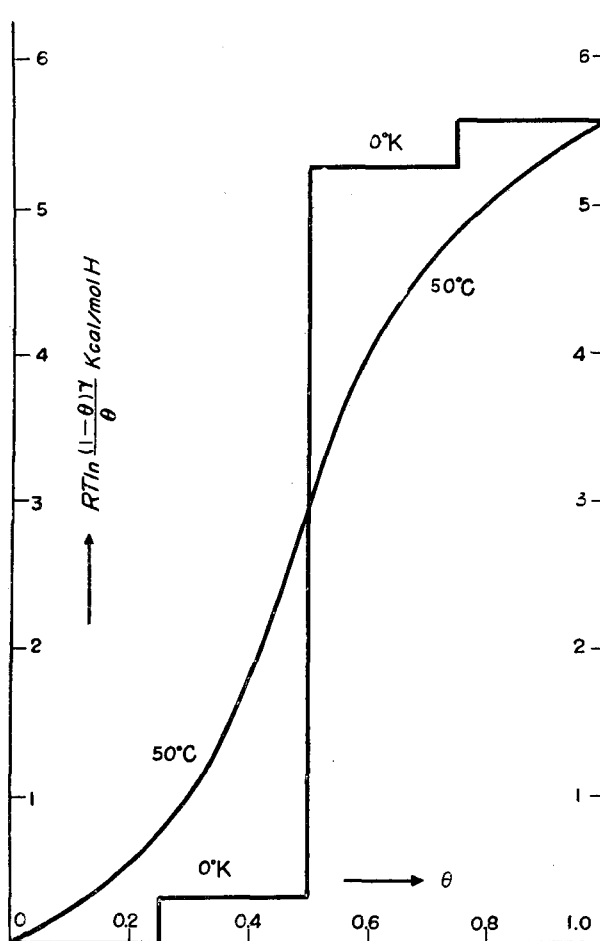


Fig. 1. Free energy of repulsion.

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  $\theta$  and compared with the tierlike dependence of  $W$  on  $\theta$  reckoned for the absolute zero temperature<sup>1)</sup>.

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

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

The present author wishes to thank Dr. T. TOYA for his kind interest to the work<sup>1)</sup> and his valuable suggestions for improvements inclusive of the present one.