INVESTIGATION OF THE DESORPTION OF DEUTERIUM FROM THE TITANIUM SPONGE

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INTRODUCTION

In the past few years great attention has been paid to the desorption os gases from the surface of various substances in the solid state. The authorf of the articles dealing with the desorption chose, for the most part, such substances as absorption solids that the given gas only adsorbed. The purpose of those papers was to confirm the theory of desorption worked out and treated by various investigators and summarized and supplemented by P. A. Redhead [1] and G. Carter [2, 3].

The aim of the present paper is to investigate the desorption from a substance (Ti-sponge) which not only adsorbs, but also absorbs a given gas (D_2), to determine the interval of activation energy from the desorption of deuterium from the Ti-sponge and to compare it with the corresponding energy values for hydrogen measured in communication [4], and to find whether it is possible to determine the desorption with the aid of the equation

$$\sum_i \frac{dn_i}{dt} = \gamma_0 \sum n_i^x \exp\left(-Q_i/RT\right) \qquad (1)$$

for $x = 1$ or for $x = 2$; where; n_i — the number of atoms sorbed by the site with energy Q_i in time t; γ_0 — constant characterizing the vibration frequency of the absorbed atoms along the normal to the absorbed surface; R — gas constant; T — temperature of the absorption solid surface.

Besides, the author also deduces the resolution of the technique used for measuring the two sites Q_i and $Q_i + \Delta Q_i$ from the discrete spectrum of activation energies in case one proceeds in the analysis of the spectrum from Eq. (1) for $x = 1$ or for $x = 2$. A similar relation for $x = 1$ was derived in paper [2].

DESCRIPTION OF MEASURING EQUIPMENT

The equipment used for measuring the desorption curves is also employed for the production of deuterium-titanium targets [5]. The functional diagram of the equipment is to be seen in Fig. 1.

The equipment consists of;

a) A high-vacuum pumping set, composed of a rotation pump — 1 and a diffusion pump — 2, a trap — 3 cooled by liquefied nitrogen.

b) A regeneration flask — 11 ending in a ground joint jacket NZ 70, the lower edge of the ground joint being ground-in forming with the flange of
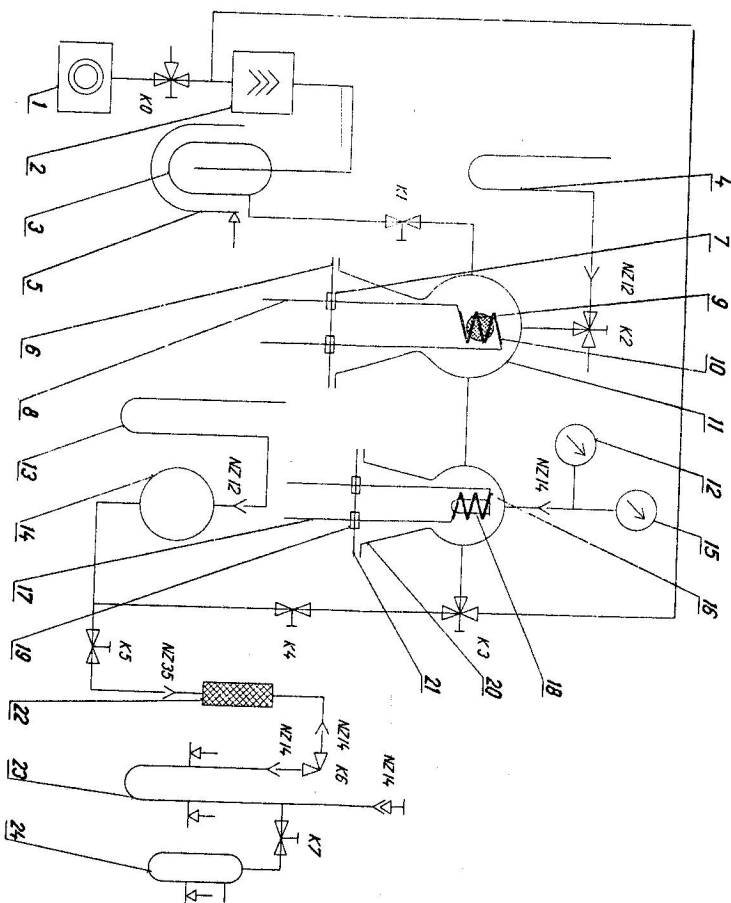

Fig. 1. Functional diagram of the equipment for measuring deuterium desorption from the Ti-sponge. 1 — rotation pump, 2 — diffusion pump, 3 — trap, 4 — oil pressure-gauge, 5 — Dewar flask, 6 — brass flange, 7 — current reducers, 8 — current supplies, 9 — target, 10 — target heating coil, 11 — regeneration flask, 12 — Penning gauge, 13 — mercury pressure-gauge, 14 — deuterium tank, 15 — resistor pressure-gauge, 16 — heating coil, 17 — current supply, 18 — Si-ampule with Ti-sponge, 19 — current reducers, 20 — Ti-absorption solid flask, 21 — brass flange, 22 — P_2O_5, 23 — electrolyzer, 24 — washing-bottle.

the flask closure — 6, via a rubber lining put in the groove of the flange, a vacuum-tight joint. In the upper part of the flask a mercury or iol pressure-gauge is connected to the vacuum system via a glass cock K 2 and a ground joint NZ 12. The glass cock K 2 permits to admit air into the regeneration flask if the vacuum system is operated only via the glass cock K 1.

c) A Ti-absorption solid flask — 20, also ending in a glass ground joint NZ 45, whose lower edge is ground-in so as to form a vacuum-tight joint with the flange of the flask closure — 21 provided with a groove for the rubber lining. In its upper part a Penning gauge — 12 of a combined vacuum meter and a Pirani pressure-gauge — 15 are located.

d) A section formed of a system of glass cocks K 3, K 4, K 5, a needle valve K 6, a deuterium tank — 14, and a deuterium purifier ending in a ground joint NZ 35. The ground glass joint is filled with P_2O_5 — 22 by which the water vapours of the admitted gas are absorbed. In the upper part of the tank bulb a mercury pressure-gauge — 13 or a thermometer of a combined vacuum meter is placed.

e) An electrolyzer — 23 composed of a glass cock K 7 and a washing bottle — 24 via which O_2 passes during the D_2O electrolysis.

f) A Ti-absorption solid heating system. The Ti-absorption solid is heated by radiant heat from an alternating current heated kanthal coil — 16. The coils are fixed in two opposite points on a ceramic rod with the aid of a piece of tungsten wire, by a Ta strip arranged so that the contact points of the coils with the Ta strip do not touch the ceramic rod directly. In the reverse case, overheating of the coil occurs in the points of contact. Along the coil of the heating system a silica ampule — 18 is placed, with a 2—3 g Ti-sponge as absorption solid. The temperature of the sponge is measured with a Ni-NiCr thermocouple via an opening made in its bottom part.

g) A target heating system arranged in the same way as the heating system described in paragraph f).

Both heating systems permit to reach temperatures of the heating units ranging between 600 and 800 °C

METHOD FOR MEASURING DESORPTION CURVES AND RESULTS OF MEASUREMENTS

Before being put in the flask — 20, the Ti-sponge was left to corrode in H_2SO_4 heated to 80—90 °C for 4 to 5 minutes, whereupon it was washed in two beakers with boiling distilled water and in two beakers with methyl alcohol. After being dried on filter paper, the sponge was put in the Ti-absorption solid flask and after exhaustion of the entire desorption space to a pressure of 10^{-5}—10^{-6} torr deaeration followed together with that of the

entire heating system for 1.5 to 2 hours. Deaeration was performed so that the pressure in the desorption space of the sponge did not exceed 5×10^{-5}—8×10^{-5} torr. After deaeration, the heating of the Ti-sponge was stopped and the sponge was allowed to cool down to room temperature under continuous operation of the rotation and diffusion pumps and cooling with liquefied nitrogen. After this, deuterium was filled into the Ti-sponge space to the required pressure (≈ 100—150 torr) from a tank — 14. Through the heat from the kanthal coil of the heating system — 16 the sponge was heated in the deuterium atmosphere to 500—600 °C. By reducing the heating current cooling to 25—50 °C the temperature of the sponge dimished through gradual natural cooling to 25—50 °C. The cooling set in only if the absorption of the sponge observed on the oil or mercury pressure-gauge, respectively. The process of reducing the temperature was repeated until a temperatures of 50 °C was reached. After cooling the sponge to room temperature, which took about 40 to 50 minutes, the pressure drop in the sorption space was measured. From this pressure drop the deuterium atomic rate (i. e. concentration) of the Ti-sponge was calculated from the relation

$$N = 4.27 \, V_n/n, \qquad (2)$$

where; m — weight of the saturated Ti-sponge in mg; V_n — amount of deuterium in ccm of the saturated sponge and converted to normal conditions.
Hence

$$V_n = \frac{V_k \varDelta p}{760} \cdot \frac{273}{273 + t'} \quad [\text{ccm}], \qquad (3)$$

where; V_k — sorption volume of the Ti-sponge: $\varDelta p$ — deuterium pressure drop in the sorption space of the Ti-sponge after its saturation: t' — room temperature.

After saturation, the sorbed deuterium from the Ti-sponge was desorbed under continuous operation of the rotation pump and cooling by liquefied nitrogen. Desorption was caused by heating the sponge to 500—600 °C. The procedure during heating was as follows: The temperature of 150 °C was reached in about 3 minutes. A further temperature rise was linear with time. Every second the temperature of the sponge rose by .5 °C. At a temperature of 550—600 °C, heating was stopped. The dependence of deuterium pressure p in the desorption space of the Ti-sponge on time t and temperature T, which were measured, is illustrated in Figs. 2 and 3. The maximum error in the measurements of pressure p was 5—10 %, while in the temperature measurements it made 2—5 %, and in the time measurements .06—.3 %. Curves 1 and 1' correspond to the desorption from a Ti-sponge of weight
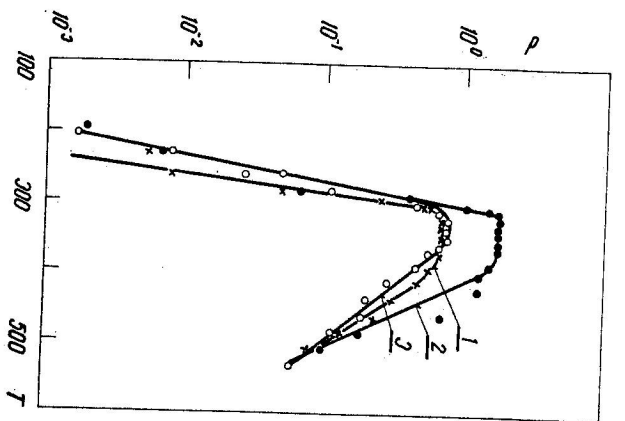

Fig. 2. Dependence of the pressure p [torr] of the desorbed deuterium on the temperature of the Ti-sponge T [°C]: 1 — deuterium desorbed from a Ti-sponge weighing $m_1 = 1.8620$ g and having the deuterium atomic rate $N_1 = .33$; 2 — deuterium desorbed from a Ti-sponge weighing $m_2 = 1.8620$ g and having the deuterium atomic rate $N_2 = .29$; 3 — deuterium desorbed from a Ti-sponge weighing $m_3 = 1.6596$ g and having the deuterium atomic rate $N_3 = .69$.
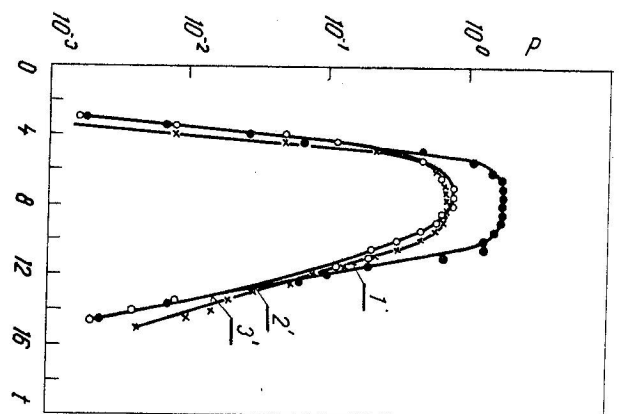

Fig. 3. Dependence of the pressure p [torr] of the desorbed deuterium from the Ti-sponge on time t [minutes]. 1' — deuterium desorbed from a Ti-sponge weighing $m_1 = 1.8620$ g and having the deuterium atomic rate $N_1 = .33$; 2' — deuterium desorbed from a Ti-sponge weighing $m_2 = 1.8620$ g and having the deuterium atomic rate $N_2 = .29$; 3' — deuterium desorbed from a Ti-sponge weighing $m_3 = 1.6596$ g and having the deuterium atomic rate $N_3 = .69$.

$m_1 = 1.8620$ g and the deuterium atomic rate $N_1 = .33$: curves 2 and 2' to the desorption from a Ti-sponge of weight $m_2 = 1.8620$ g and $N_2 = .29$, and curves 3 and 3' to the desorption from a Ti-sponge of weight $m_3 = 1.6596$ g and $N_3 = .69$. From the measured dependences $p = p(t)$ the curves of the desorption rate $N/N_m = f(t, T)$ were calculated, where $N = (- dn_i/dt)$, $N_m = (- dn_i/dt)_{T_m}$ and T_m — temperature at which the desorption rate N/N_m is maximum. In the calculation we assumed that the desorption rate $\varDelta t$ is longer in comparison with the characteristic pumping time τ [1]. This assumption was confirmed by our measurements; $\varDelta t \approx 12$ minutes, $\tau \approx 2 \rightarrow$ $\rightarrow \varDelta t > \tau$. According to [1] it follows that $N/N_m \approx p)/p_{max}$.
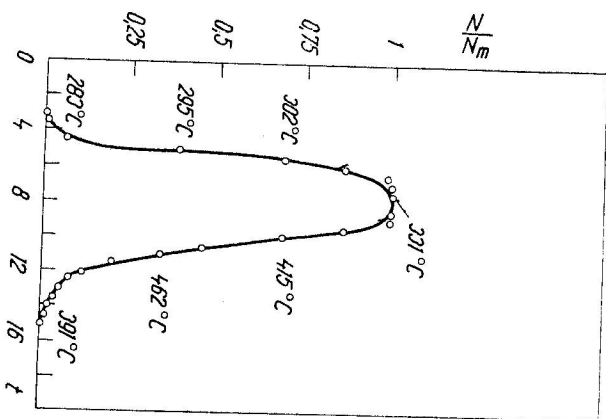
Fig. 4. Dependence of the desorption rate N/N_m [rate units] on the time t [minutes], calculated from the pressure values plotted in Figs 2 (1) and 3 (1').
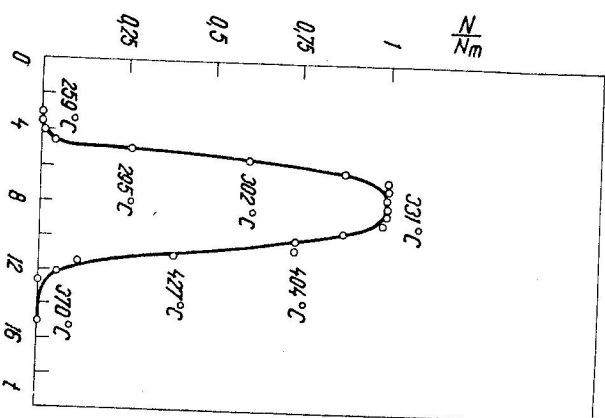

Fig. 5. Dependence of the desorption rate N/N_m [rate units] on the time t [minutes], calculated from the pressure values plotted in Figs 2 (2) and 3 (2').
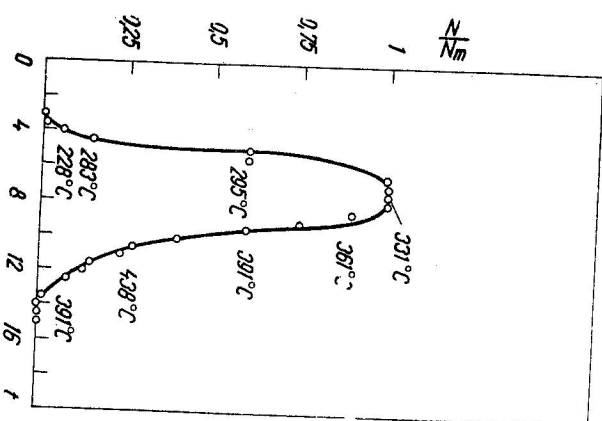
In Fig. 4 the normalized desorption rate calculated from the pressure values plotted in Fig. 2 (1) and Fig. 3 (1') is illustrated: in Fig. 5 the normalized desorption rate calculated from the pressure values plotted in Fig. 2 (2) and Fig. 3 (2'), while in Fig. 6 the normalized desorption rate calculated from the pressure values plotted in Fig. 2 (3) and Fig. 3 (3'). In the measurements we also assumed that:

1. No adsorption occurs in the desorption cycle in the very Ti-sponge,
2. sorption on the wall of the Ti-absorption solid flask is negligible,
3. sorption in the individual parts of the heating system is negligible.

RESULTS AND DISCUSSION

When elucidating the physical principle of desorption, we proceed from the fact that the atoms of the sorbed gas in the sorbent bind a certain energy Q_t given in kcal/mol. This energy is called activation energy of sorption and activation energy of desorption, respectively. The lowest value of this energy

Fig. 6. Dependence of the desorption rate N/N_m [rate units] on the time t [minutes], calculated from the pressure values plotted in Figs 2 (3) and 3 (3').

for the lowest concentration of hydrogen sorbed in Ti is 19 kcal/mol [4]. With increasing hydrogen concentration, its value rises, but only in those cases where the shape of the Ti crystal lattice corresponds to the α-phase [6].

In the Ti two-phase region the energy Q_t does not depend on the concentration. The energy value in this region depends only on the temperature. With the temperature rising it increases from 27 to 43 kcal/mol. In the β region, its value also rises with the temperature from 26 to 44 kcal/mol. We may assume that a similar range of values of binding energies holds also good for deuterium sorbed in Ti. From the desorption curves illustrated in Figs 4 to 6 it follows that the maximum amount of sorbed deuterium ($\approx$ 80 %) is desorbed in the temperature range between 200 and 500 °C. The lowest temperature at which desorption could be identified was thus 200 °C. To this temperature there corresponds an activation energy [1] — from the dependence $Q_t = f(\beta, T_m)$, for $\beta = 1$ °K/s — corresponds the value $Q_t = 30$ kcal/mol. To the temperature of 500 °C there corresponds the value $Q_t = 47$ kcal/mol. From the course of the desorption curves it is also evident that if for the temperature at which the maximum desorption occurs we take the value of 331 °C, desorption from the deuterium-saturated Ti-sponge can be determined by Eq. (1) for $x = 1$. From the measurements it follows that maximum desorption occurs most probably at the temperature of 331 °C.

The spectrum of activation energy Q_t can be continuous or discrete. In

the analysis of the desorption spectrum performed for the case of discrete distribution of activation energies it is necessary to know the resolution power of the measuring technique. According to [2], the value of this resolution can be characterized by the ration $Q_t/\Delta Q_t$. For $x = 1$ (see Appendix I) we have for the resolution value:

$$\frac{Q_t}{\Delta Q_t} = \frac{1 - 3.6RK}{3RK};$$ (4)

for $x = 2$ (see Appendix II);

$$\frac{Q_t}{\Delta Q_t} = \frac{1 - 4.2RK}{4.2RK},$$ (5)

where K — constant, $K \in \langle 14.8; 18.5 \rangle$ °K mol/kcal, for $\beta \in \langle 1; 1000 \rangle$ °K/s ($\beta = dT/dt$ — heating rate.)

If $RK \approx 3 \times 10^{-2}$, we obtain for $x = 1$ the valu 10.2 and for $x = 2$ the value 6.9. For $Q_t = 40$ kcal/mol e. g. the difference between the sites we can distinguish is in the case of $x = 1$ 3.9 kcal/mol, and in the case of $x = 2$ it is 5.8 kcal/mol.

ΔQ_t diminishes if RK and β, respectively, increase. To obtain a higher ΔQ_t between the sites, it is more advantageous to heat the sample on which the desorption is tested with a low β rather than with a high one. From [1] it follows that the value of the maximum desorption rate N_m is proportional to β. Diminution of β thus leads to a low desorption rate. In this case it is necessary to measure the desorption with a more sensitive apparatus. In order to be able to measure the desorption, we must make a compromise between sensitivity and the desorption rate.

CONCLUSION

With the aid of known methods we investigated the desorption properties of the Ti-sponge saturated with deuterium. From the course of the measured desorption curves it could be concluded that the maximum amount of sorbed deuterium ($\approx 80\%$) is desorbed in a temperature range of 200 to 500 °C. To this range correspond according to [1] from the dependence $Q_t = f(\beta, T_m)$, for $\beta = 1$ °K/s activation energies of 30—47 kcal /mol. From the course of the desorption curves it can also be seen that if we take for the temperature, at which the maximum desorption occurs, the value of 331 °C (from the temperature, at which the maximum desorption occurs, the value of 331 °C (from the measurements it follows that the maximum desorption occurs most probably at 331 °C), the desorption from the deuterium-saturated Ti-sponge can be determined by Eq. (1) for $x = 1$.

242

Besides, the method of deducing the relations characterizing the resolution power of the measuring technique for $x = 1$ and $x = 2$, is delt with. It has been found that the relation for resolution, derived for $x = 1$ in communication [2], can be approached by introducing $(1 - .8RK)$ instead of $\sqrt{D_1}$ in Eq. (19a). From the relation for the resolution of the measuring technique it follows that for $Q_t = 40$ kcal/mol and $RK \approx 3 \times 10^{-2}$ the difference between the sites that can be resolved from each other is 3.9 kcal/mol for $x = 1$, while 5.8 kcal/mol for $x = 2$.

APPENDIX I

Let T_e be the temperature at which the desorption rate $N_e = e^{-1}N_m$, for a site with the energy Q_i (maximum desorption rate being at temperature T_m) and $T_{e'}$ and $T_{m'}$ the corresponding temperatures for a site with the energy $Q_i + \Delta Q_t$. According to Fig. 7, giving the typical dependences of the desorption rate on temperature (on time), we get for the two energies Q_i and $Q_i + \Delta Q_t$;

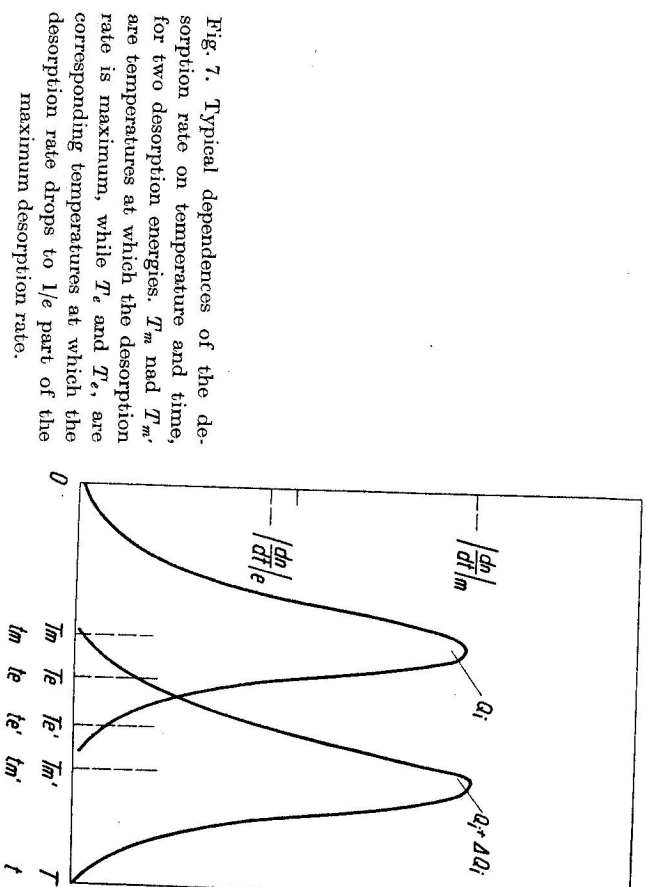$$(T_e - T_m) + (T_{m'} - T_{e'}) \ll (T_{m'} - T_m),$$ (6a)

Fig. 7. Typical dependences of the desorption rate on temperature and time, for two desorption energies. T_m nad $T_{m'}$ are temperatures at which the desorption rate is maximum, while T_e and $T_{e'}$ are corresponding temperatures at which the desorption rate drops to 1/e part of the maximum desorption rate.

243

or

$$\Delta t_{em} + \Delta t_{m'e'} \ll \Delta t_{m'm}, \quad (6b)$$

respectively.

Let n_0 be the total number of atoms sorbed by a site with the energy Q_t. Then, through the integration of the left-hand side of Eq. (1) for $x = 1$ from n_0 to n_t, and of the right-hand side from T_0 to T, we obtain for one energy site Q_t and for $T = T_0 + \beta t$, if we consider that (see [1])

$$\frac{\gamma_0}{\beta} \int_{T_0}^{T} \exp(-Q_t/RT)\, dT = \frac{\gamma_0 R}{\beta Q_t}[T^2 \exp(-Q_t/RT) - T_0^2 \exp(-Q_t/RT_0)], \quad (7)$$

the equation

$$\frac{dn_t}{dt} = -\gamma_0 n_{t0} \exp(-Q_t/RT) \exp\left\{-\frac{\gamma_0 R}{\beta Q_t}[T^2 \exp(-Q_t/RT) - T_0^2 \exp(-Q_t/RT_0)]\right\}.$$

Hence for the desorption rate at temperature T_m;

$$\left(\frac{dn_t}{dt}\right)_m = -\gamma_0 n_{t0} \exp(-Q_t/RT_m) \exp\left\{-\frac{\gamma_0 R}{\beta Q_t}\right.$$
$$\times [T_m^2 \exp(-Q_t/RT_m) - T_0^2 \exp(-Q_t/RT_0)]\Big\},$$

and at the temperature T_e

$$\left(\frac{dn_t}{dt}\right)_e = -\gamma_0 n_{t0} \exp(-Q_t/RT_e) \exp\left\{-\frac{\gamma_0 R}{\beta Q_t} \times\right.$$
$$\times [T_e^2 \exp(-Q_t/RT_e) - T_0^2 \exp(-Q_t/RT_0)]\Big\}.$$

Since $(dn_t/dt)_e = e^{-1}(dn_t/dt)_m$, we get through substitution of the already mentioned rates, neglection of $T_0^2 \exp(-Q_t/RT_0)$ against $T_m^2 \exp(-Q_t/RT_m)$, and through logarithmic calculation upon adjustment;

$$-\frac{Q_t}{RT_m} + \frac{Q_t}{RT_e} = 1 - \frac{\gamma_0 R}{\beta Q_t}[T_e^2 \exp(-Q_t/RT_e) - T_m^2 \exp(-Q_t/RT_m)]$$

respectively

$$\frac{Q_t}{R}\left(\frac{1}{T_e} - \frac{1}{T_m}\right) = 1 - \frac{\gamma_0 R}{\beta Q_t} T_m^2 \exp(-Q_t/RT_m) \times$$
$$\times \{[T_e/T_m]^2 \exp[(T_m^{-1} - T_e^{-1})Q_t/R] - 1\}. \quad (8)$$

By solving Eq. (1) for the maximum desorption rate and for $x = 1$, we obtain

$$T_m^2 \exp(-Q_t/RT_m) = Q_t \beta/R\gamma_0. \quad (9)$$

Through substitution into (8) and the introduction of substitution

$$z = (T_m^{-1} - T_e^{-1})Q_t/R$$

and

$$(T_e/T_m)^2 \approx (T_m^{-1} - T_e^{-1})2T_m + 1 = zT_m 2R/Q_t + 1$$

we obtain

$$-z = 2 - (T_m z\, 2R/Q_t + 1)e^z. \quad (10)$$

According to [1]

$$T_m = KQ_t \quad (11)$$

for $\beta \in \langle 1: 1000 \rangle$ °K/s.
Through substitution of (11) into (10) we obtain

$$-z = 2 - (2RKz + 1)e^z,$$

or

$$z + 2 = e^z(2RKz + 1), \quad (12)$$

respectively.

$R \approx 2 \times 10^{-3}$ kcal/°K mol: for K, if we take the value 15, $RK \approx 3 \times 10^{-2}$. We may thus assume that $1 \gg 2RK|z|$. Eq. (12) is then reduced to the equation

$$z + 2 = e^z,$$

through a graphical solution of which we may obtain the values of z,

$$z_1 \approx +1.2 \quad \text{and} \quad z_2 \approx -1.8.$$

Thus there exist two temperatures T_{e_1} and T_{e_2}, before and after temperature T_m. Their values can be calculated from the following equation:

$$T_m^{-1} - T_{e_1}^{-1} = 1.2R/Q_t \quad \text{and} \quad T_{e_2}^{-1} - T_m^{-1} = 1.8R/Q_t.$$

From the equation for z and from the equation for $T = T_0 + \beta t$ we obtain:

$$z = \frac{Q_i}{R} \Delta \left(\frac{1}{T_{me}}\right) \approx \frac{Q_i}{R} \cdot \frac{T_e - T_m}{T_m^2} = \frac{Q_i}{R} \cdot \frac{\beta \Delta t_{em}}{T_m^2}.$$

For the energy Q_i:

$$\Delta t_{em} = 1.2 R T_m^2 / \beta Q_i$$ (13a)

and for the energy $Q_i + \Delta Q_i$:

$$\Delta t_{m'e'} = 1.8 R T_m^2 / \beta (Q_i + \Delta Q_i).$$ (13b)

Whence

$$\Delta t_{em} + \Delta t_{m'e'} = (3Q_i + 1.8\Delta Q_i) R T_m^2/\beta.$$ (14)

$\Delta t_{m'm}$ can be derived from the equations for the maximum desorption rate for sites with the energies Q_i and $Q_i + \Delta Q_i$.

According to (9)

$$\exp(-Q_i/RT_m) = \beta Q_i/\gamma_0 R T_m^2,$$

and for sites with the energies

$$\exp[-(Q_i + \Delta Q_i)/RT_{m'}] = \beta(Q_i + \Delta Q_i)/\gamma_0 R T_{m'}^2.$$ (15)

Dividing the second equation by the first and considering that

$$(1 + \Delta Q_i/Q_i)(T_m/T_{m'})^2 \approx \exp[(T_m/T_{m'})^2 \Delta Q_i/Q_i],$$

we obtain through logarithmic calculation of both sides and after adjustment;

$$-(T_{m'}^{-1} - T_m^{-1})Q_i/R - \Delta Q_i/RT_m = (\Delta Q_i/Q_i)(T_m/T_{m'}).$$ (16)

If instead of $(T_m/T_{m'})^2$ we introduce similarly as in the adjustment of Eq. (8) the relation

$$(T_m/T_{m'})^2 \approx -2(T_m^{-1} - T_{m'}^{-1})T_m + 1,$$

we obtain through the adjustment of Eq. (16)

$$T_{m'} - T_m = T_m(\Delta Q_i/Q_i)(Q_i + RT_m)/(Q_i + 2RT_m \Delta Q_i/Q_i),$$ (17a)

respectively

$$\Delta t_{m'm} = (K\Delta Q_i/\beta)[1 + RK(1 + \Delta Q_i/Q_i)]/(1 + 2RK\Delta Q_i/Q_i).$$ (17b)

Through comparison of Eqs (6), (14) and (17b) we obtain the expression for the site of the resolution value $Q_i/\Delta Q_i$. Hence the following holds:

$$3RK + 1.8(\Delta Q_i/Q_i)RK + 6R^2K^2(\Delta Q_i/Q_i) + 3.6R^2K^2(\Delta Q_i/Q_i)^2 =$$
$$= (\Delta Q_i/Q_i) + RK(\Delta Q_i/Q_i) + RK(\Delta Q_i/Q_i)^2,$$ (18a)

respectively

$$RK(3.6RK - 1)(\Delta Q_i/Q_i)^2 + (6R^2K^2 + .8RK - 1)(\Delta Q_i/Q_i) + 3RK = 0.$$ (18b)

The solution of the quadratic equation leads to two roots, one of which is positive and the other one negative. For the discriminant of the Eq. (18b) we can write

$$D_1 = (6R^2K^2 + .8RK - 1)^2 - 12R^2K^2(3.6RK - 1).$$

Since $\Delta Q_i/Q_i > 0$, $\sqrt{D_1} > (1 - .8RK - 6R^2K^2)$ and the term in $(\Delta Q_i/Q_i)^2$ is negative, i. e. $RK(3.6RK - 1) < 0$ for all values $K \in \langle 14.8; 18.5 \rangle$ °K mol/kcal;

$$Q_i/\Delta Q_i = 2RK(3.6RK - 1)/\{-(6R^2K^2 + .8RK - 1) -$$
$$-[(6R^2K^2 + .8RK - 1)^2 - 12R^2K^2(3.6RK - 1)]^{1/2}\}.$$ (19a)

For $RK \approx 3 \times 10^{-2}$ we have $\sqrt{D_1} = .9517$ and $(1 - .8RK) = .9760$. If instead of $\sqrt{D_1}$ we introduce the expression $(1 - .8RK)$, we obtain for the resolution:

$$Q_i/\Delta Q_i = (1 - 3.6RK)/3RK.$$ (19b)

The derived relation (19b) is identical with the relation (4).

APPENDIX II

Similarly as in Appendix I, through integration of the left-hand side of Eq. (1) for $x = 2$ from n_{i0} to n_i and of the right-hand side from T_0 to T, for one energy site Q_i and for $T = T_0 + \beta t$, we obtain if we consider the validity of Eq. (7) and the equation for the maximum desorption rate in this case, i. e. equation $N_m = n_{i0}\beta Q_i/4RT_m^2$,

$$\frac{dn_i}{dt} = -\frac{n_{i0}\beta Q_i}{4RT_m^2} 4\{\exp[(-Q_i/2R)(T_m^{-1} - T^{-1})] + (T/T_m)^2 \times$$
$$\times \exp[(Q_i/2R)(T^{-1} - T_m^{-1})]\}^{-2}.$$ (20)

From the identity $(dn_i/dt)_e = e^{-1}(dn_i/dt)_m$ and from the expressions for $(dn_i/dt)_e$ and $(dn_i/dt)_m$ derived from Eq. (20) we obtain through the introduction of $T \to T_e$ and $T \to T_m$

$$e^{-1} = 4\{\exp[(-Q_i/2R)(T_m^{-1} - T_e^{-1})] + (T_e/T_m)^2 \exp[(Q_i/2R) \times$$
$$\times (T_m^{-1} - T_e^{-1})]\}^{-2},$$

respectively

Since $(T_e/T_m)^2 \approx 2RKz + 1$ and $(T_e/T_m)^4 \approx (2RKz + 1)^2$, we can rewrite (21) in the form;

$$4e = 2(2RKz + 1) + \exp(-z) + (2RKz + 1)^2 \exp(z).$$

If $2RK|z| \ll 1$, we obtain after adjustment and introduction of the substitution $y = e^z$.

$$y^2 - 2(2e - 1)y + 1 = 0.$$

The solution of the quadratic equation leads to the roots

$$y_1 = (2e - 1) + 2\sqrt{e(e - 1)} \approx 8.7,$$
$$y_2 = (2e - 1) - 2\sqrt{e(e - 1)} \approx .12.$$

Whence

$$z_1 = \ln y_1 \approx 2.1,$$
$$z_2 = \ln y_2 \approx -2.1.$$

Unlike in the preceding case, it is to be seen that the values z_1 and z_2 are symmetrically distributed with respect to the zero point z.

Thence

$$(Q_i/R)(T_m^{-1} - T_e^{-1}) = 2.1 \quad \text{or} \quad -2.1$$

and

$$\Delta t_{em} = 2.1RT_m^2/\beta Q_i; \quad \Delta t_{m'e'} = 2.1RT_m^2/\beta(Q_i + \Delta Q_i).$$

Whence

$$\Delta t_{em} + \Delta t_{m'e'} = 2.1RK^2(2Q_i + \Delta Q_i)/\beta. \tag{22}$$

$\Delta t_{m'm}$ is derived from the equations for the maximum desorption rate for sites with energies Q_i and $Q_i + \Delta Q_i$. For $x = 2$ we obtain through derivation of Eq. (1) with respect to time, through annulment of the equation and upon adjustment:

$$\exp(-Q_i/RT_m) = (Q_i/\gamma_0RT_m^2)(\beta/n_{i0}),$$

$$\exp[-(Q_i + \Delta Q_i)/RT_m'] = [(Q_i + \Delta Q_i)/\gamma_0RT_m'^2](\beta/n_{i0}'),$$

where n_{i0}' is the total number of atoms sorbed by the site $Q_i + \Delta Q_i$. Let

us assume that $n_{i0} = n_{i0}'$, dividing the second equation by the first and considering that

$$(1 + \Delta Q_i/Q_i)(T_m/T_m')^2 \approx \exp[(\Delta Q_i/Q_i)(T_m/T_m')^2]$$

we obtain through logarithmic calculation of both sides an equation which is identical with Eq. (17a). In this case ($x = 2$) the relation for $\Delta t_{m'm}$ is identical with relation (17b). Through comparison of Eqs (6), (22) and (17b) we obtain the expression for the resolution value $Q_i/\Delta Q_i$. Hence

$$2.1(2Q_i + \Delta Q_i)K^2R/\beta = (K\Delta Q_i/\beta)[1 + RK(1 + \Delta Q_i/Q_i)]/(1 + 2RK\Delta Q_i/Q_i),$$

or

$$4.2RK + 8.4R^2K^2\Delta Q_i/Q_i + 2.1RK\Delta Q_i/Q_i + 4.2R^2K^2(\Delta Q_i/Q_i)^2 =$$

$$= \Delta Q_i/Q_i + RK\Delta Q_i/Q_i + RK(\Delta Q_i/Q_i)^2, \tag{23a}$$

respectively

$$RK(4.2RK - 1)(\Delta Q_i/Q_i)^2 + (8.4R^2K^2 + 1.1RK - 1) \times$$

$$\times (\Delta Q_i/Q_i) + 4.2RK = 0. \tag{23b}$$

The solution of the quadratic equation leads, similarly as in Appendix I, to two roots, one of which is positive the other negative. For the discriminant of Eq. (23b) we can write

$$D_2 = (8.4R^2K^2 - 1)(\Delta Q_i/Q_i)^2 + (8.4R^2K^2 - 1)^2 - 16.8R^2K^2(4.2RK - 1).$$

Since $\Delta Q_i/Q_i > 0$, $\sqrt{D_2} > (1 - 1.1RK - 8.4R^2K^2)$ and the term in $(\Delta Q_i/Q_i)^2$ is negative, i. e. $RK(4.2RK - 1) < 0$ for all values $K \in < 14.8: 18.5 >$ °K mol/kcal, we can write

$$Q_i/\Delta Q_i = 2RK(4.2RK - 1)/\{- (8.4R^2K^2 + 1.1RK - 1) -$$

$$- [(8.4R^2K^2 + 1.1RK - 1)^2 - 16.8R^2K^2(4.2RK - 1)]^{1/2}\}.$$

For $RK \approx 3 \times 10^{-2}$ we have $\sqrt{D_2} = .9337$ and $(1 - 1.1RK) = .9670$. If we introduce the expression $(1 - 1.1RK)$ instead of $\sqrt{D_2}$ for the resolution, we obtain

$$Q_i/\Delta Q_i = (1 - 4.2RK)/4.2RK. \tag{24}$$

The derived relation (24) is identical with relation (5).

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