Physics 880.20
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Answers To Assignment 4

(1) $k_{dis} = \nu e^{-E_D/kT}$ $\quad \frac{dN_A}{dt} = -k_{dis} N_A$

$N_A(t) = N_A(0) e^{-k_{dis} t}$

$$\langle t \rangle = \frac{\int_0^\infty t\, e^{-k_{dis} t}\, dt}{\int_0^\infty e^{-k_{dis} t}\, dt} = k_{dis}^{-1} = \nu^{-1} e^{E_D/kT}$$

$\langle r^2 \rangle^{1/2} = \left(d^2 k_{hop} \langle t \rangle \right)^{1/2}$ $\quad k_{hop} = \nu e^{-E_b/kT}$

$$= \left(d^2 e^{(E_D - E_b)/kT} \right)^{1/2}$$

$D_D = \nu d^2/4$, so $\langle r^2 \rangle^{1/2} = \left(\frac{4 D_D}{\nu} e^{(E_D - E_b)/kT} \right)^{1/2}$

(2) $k_{ads}^{\sigma} = \langle S_0(v) v_\perp \rangle = \frac{1}{4} \int_{v_{min}}^{\infty} v\, P(v)\, dv$

$E_a = \frac{1}{2} m v_{min}^2$

$E = \frac{1}{2} m v^2$

Switch to E: $f(E)\,dE = P(v)\,dv$

$$k_{ads}^{\sigma} = \frac{1}{4} \int_{E_a}^{\infty} \left(\frac{2E}{m} \right)^{1/2} f(E)\, dE$$

$$f(E)\,dE = \frac{2}{\sqrt{\pi}} E^{1/2} (k_B T)^{-3/2} e^{-E/k_B T}$$

$$k_{ads}^{\sigma} = \frac{1}{4} \int_{E_a}^{\infty} \left(\frac{2}{m} \right)^{1/2} \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} E\, e^{-E/k_B T}\, dE$$

$\epsilon = E - E_a$; $k_{ads}^{\sigma} = \frac{1}{2} \sqrt{\frac{2}{m\pi}} \frac{1}{(k_B T)^{3/2}} \int_0^\infty (\epsilon + E_a) e^{-[\epsilon + E_a]/kT}\, d\epsilon$

$$k_{ads}^{\sigma} = \sqrt{\frac{1}{2m\pi}} \frac{1}{(k_B T)^{3/2}} e^{-E_a/k_B T} \underbrace{\int_0^\infty (\epsilon + E_a) e^{-\epsilon/kT}\, d\epsilon}_{I}$$

$$I = \underbrace{\int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon}_{(kT)^2} + E_a \underbrace{\int_0^\infty e^{-\epsilon/kT} d\epsilon}_{E_a kT}$$

$$I = (kT)[kT + E_a] \approx kT E_a \quad \text{if } kT < E_a$$

$$k_{ads}^{\sigma} = \sqrt{\frac{1}{2m\pi}} \frac{1}{\sqrt{k_B T}} e^{-E_a/k_B T} E_a$$

$$\langle v_\perp \rangle = \sqrt{\frac{k_B T}{2\pi m}}$$

$$k_{ads}^{\sigma} = \langle v_\perp \rangle \frac{E_a}{k_B T} e^{-E_a/k_B T}$$

More generally:

$$k_{ads}^{\sigma} = \langle v_\perp \rangle \left(1 + \frac{E_a}{k_B T}\right) e^{-E_a/k_B T}$$

$E_a \ll k_B T \quad k_{ads}^{\sigma} \to \langle v_\perp \rangle e^{-E_a/k_B T}$

(3) $K_p = \dfrac{k_{ads}^{\theta\prime}}{k_{des}} \qquad k_{ads}^{\theta\prime} = \frac{1}{kT} k_{ads}^{\theta} = \frac{1}{kT} \frac{k_{ads}^{\sigma}}{\sigma_0}$

$$k_{des} = \nu e^{-(E_a + E_D)/k_B T}$$

$$\therefore K_p = \frac{1}{kT} \frac{\langle v_\perp \rangle (1 + E_a/k_B T) e^{-E_a/k_B T}}{\sigma_0 \nu e^{-E_a/k_B T} e^{-E_D/k_B T}}$$

$$K_p = \frac{1}{kT} \frac{\langle v_\perp \rangle}{\sigma_0 \nu} (1 + E_a/k_B T) e^{E_D/k_B T}$$

4. $E_b/k = 287\,K$ $\quad k^{H-H}_{reac,\theta} = 2\nu e^{-E_b/kT} = 6\times10^{12}\,s^{-1}\, e^{-287/T}$

$T = 100\,K \quad k^{H-H}_{reac,\theta} = 3.4\times10^{11}\,s^{-1}$

$$\frac{d\theta_H}{dt} = 1\,s^{-1} - k^{H-H}_{reac,\theta}\,\theta_H^2 = 0$$

$$\theta_H^2 = \frac{1}{k^{H-H}_{reac,\theta}} = 2.94\times10^{-12} \qquad \theta_H = 1.71\times10^{-6}\ ML$$

5. $k_{des} = \nu\, e^{-E_D/kT} = (3\times10^{12}\,s^{-1})\, e^{-300/T}$ for H_2

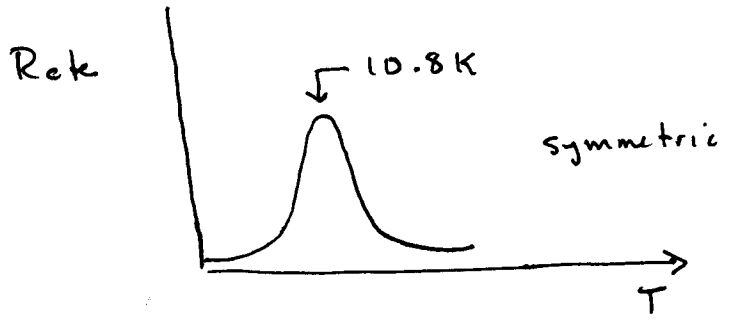
$k_{des}(10\,K) = 0.28\,s^{-1}$ $\qquad k_{des}(300\,K) = 1.1\times10^{12}\,s^{-1}$

$k_{des}(100\,K) = 1.49\times10^{11}\,s^{-1}$

TPD 1^{ST} order $\quad \frac{\nu}{\beta} e^{-E_D/kT_p} = \frac{E_D}{kT_p^2}$

$\beta = 1\,K\,s^{-1}$
$E_D/k = 300\,K$ $\qquad (3\times10^{12})\, e^{-300/T_p} = 300/T_p^2$
$\nu = 3\times10^{12}\,s^{-1}$

$T_p \approx 10.8\,K$ independent of coverage



$\beta = 5\,K\,s^{-1}$ $\qquad (6\times10^{11})\, e^{-300/T_p} = 300/T_p^2$

$T_p \sim 11.4\,K$

6. $\langle r^2\rangle^{1/2} = (d^2 k_{hop} t)^{1/2} = (d^2 N)^{1/2} = d(N)^{1/2}$

N hops in random direction. $t = 1\ hr = 3600\,s$

Area $\cong \pi \langle r^2\rangle$ $\qquad d = 3\ \text{Å}$

Use more exact expression for k_{hop} given 10 K example.

$$k_{hop} = \frac{kT}{h}\left(1 - e^{-h\nu/kT}\right) e^{-287/T} \qquad \nu = 3 \times 10^{12}\ s^{-1}$$

T(K)	k_{hop} (s^{-1})	$N = k_{hop} t$	$\langle r^2 \rangle^{1/2}$	Area
10	0.072	258 steps	48 Å	7238 $Å^2$
100	9.0×10^{10}	3.2×10^{14}	0.537 cm	0.906 cm^2
300	9.2×10^{11}	3.3×10^{15}	1.723 cm	9.327 cm^2