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1. $J = -D\nabla C$ ， $\frac{\partial C}{\partial t} = \cancel{D\nabla\cdot\nabla}\ \nabla^2 DC$

① 在球坐标中： ~~将其代入~~ $\nabla = \vec{e_r}\frac{\partial}{\partial r} + \vec{e_\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \vec{e_\varphi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$

$$\nabla^2 = \nabla\cdot\nabla = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

∴ 菲克第二定律为： $\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C}{\partial r}\right) + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(D\sin\theta\frac{\partial C}{\partial\theta}\right)\right) + \frac{1}{r^2}\left(\frac{D}{\sin^2\theta}\frac{\partial^2 C}{\partial\varphi^2}\right)$

$$= \frac{D}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial C}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial C}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 C}{\partial\varphi^2}\right)$$

② 在柱坐标系中 $\frac{\partial f}{\partial x} = \frac{\partial f}{\partial\rho}\frac{\partial\rho}{\partial x} + \frac{\partial f}{\partial\varphi}\frac{\partial\varphi}{\partial x} = \frac{\partial f}{\partial\rho}\cos\varphi - \frac{\partial f}{\partial\varphi}\frac{\sin\varphi}{\rho}$

$$\frac{\partial f}{\partial y} = \frac{\partial f}{\partial\rho}\cdot\frac{\partial\rho}{\partial y} + \frac{\partial f}{\partial\varphi}\frac{\partial\varphi}{\partial y} = \frac{\partial f}{\partial\rho}\sin\varphi + \frac{\partial f}{\partial\varphi}\frac{\cos\varphi}{\rho}$$

$$\therefore \frac{\partial^2 f}{\partial x^2} = \frac{\partial\rho}{\partial x}\frac{\partial}{\partial\rho}\left(\frac{\partial f}{\partial x}\right) + \frac{\partial\varphi}{\partial x}\frac{\partial}{\partial\varphi}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial\rho^2}\cos^2\varphi - \frac{\partial^2 f}{\partial\rho\partial\varphi}\frac{2\sin\varphi\cos\varphi}{\rho} + \frac{\partial^2 f}{\partial\varphi^2}\frac{\sin^2\varphi}{\rho^2} + \frac{\partial f}{\partial\rho}\frac{\sin^2\varphi}{\rho} + \frac{\partial f}{\partial\varphi}\frac{2\sin\varphi\cos\varphi}{\rho^2}$$

同理，$\frac{\partial^2 f}{\partial y^2} = \frac{\partial^2 f}{\partial\rho^2}\sin^2\varphi + \frac{\partial^2 f}{\partial\rho\partial\varphi}\frac{2\sin\varphi\cos\varphi}{\rho} + \frac{\partial^2 f}{\partial\varphi^2}\frac{\cos^2\varphi}{\rho^2} + \frac{\partial f}{\partial\rho}\frac{\cos^2\varphi}{\rho} - \frac{\partial f}{\partial\varphi}\frac{2\sin\varphi\cos\varphi}{\rho^2}$

$$\therefore \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \nabla^2 f = \frac{\partial^2 f}{\partial\rho^2} + \frac{\partial^2 f}{\partial\varphi^2}\frac{1}{\rho^2} + \frac{\partial f}{\partial\rho}\cdot\frac{1}{\rho} + \frac{\partial^2 f}{\partial z^2}$$

∴ 菲克第二定律为 $\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial\rho^2} + \frac{\partial^2 C}{\partial\varphi^2}\cdot\frac{1}{\rho^2} + \frac{\partial C}{\partial\rho}\cdot\frac{1}{\rho} + \frac{\partial^2 C}{\partial z^2}\right) = D\left(\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial C}{\partial\rho}\right) + \frac{\partial^2 C}{\partial\varphi^2}\frac{1}{\rho^2} + \frac{\partial^2 C}{\partial z^2}\right)$

2. 由俣野方法：$D(C) = -\frac{1}{2t}\left(\frac{dx}{dC}\right)_C\int_{C_1}^{C} x\,dC$

柱坐标中，若假定了轴对称的扩散，则有 $\frac{\partial C}{\partial t} = \frac{\partial}{\partial\rho}\left(D\frac{\partial C}{\partial\rho}\right)$

由稳态扩散： $\frac{\partial C}{\partial t} = 0 \Rightarrow D(C)\cdot\frac{dC}{d\rho} = k\cdot\text{const}$

ρ/cm	$w(C)$/%	$\frac{dC}{d\rho}/m^{-1}$	$D(C)$
0.553	0.28	−13.84	0.8024
0.540	0.46	−14.62	0.7602
0.527	0.65	−15.45	0.7189
0.516	0.82	−10.8	1.0287
0.491	1.09	−9.17	1.2121
0.479	1.20	−9.23	1.2037
0.466	1.32	−5.88	1.8888
0.449	1.42	−5.88	

取 $\rho = 0.516$ cm 处

$S = 2\pi\rho\cdot L = 3.24\times10^{-3}m^2$

$J = \frac{dm}{S\,dt} = \frac{3.6g}{3.24\times10^{-3}m^2\times100h} = 11.11g/(m^2\cdot h)$

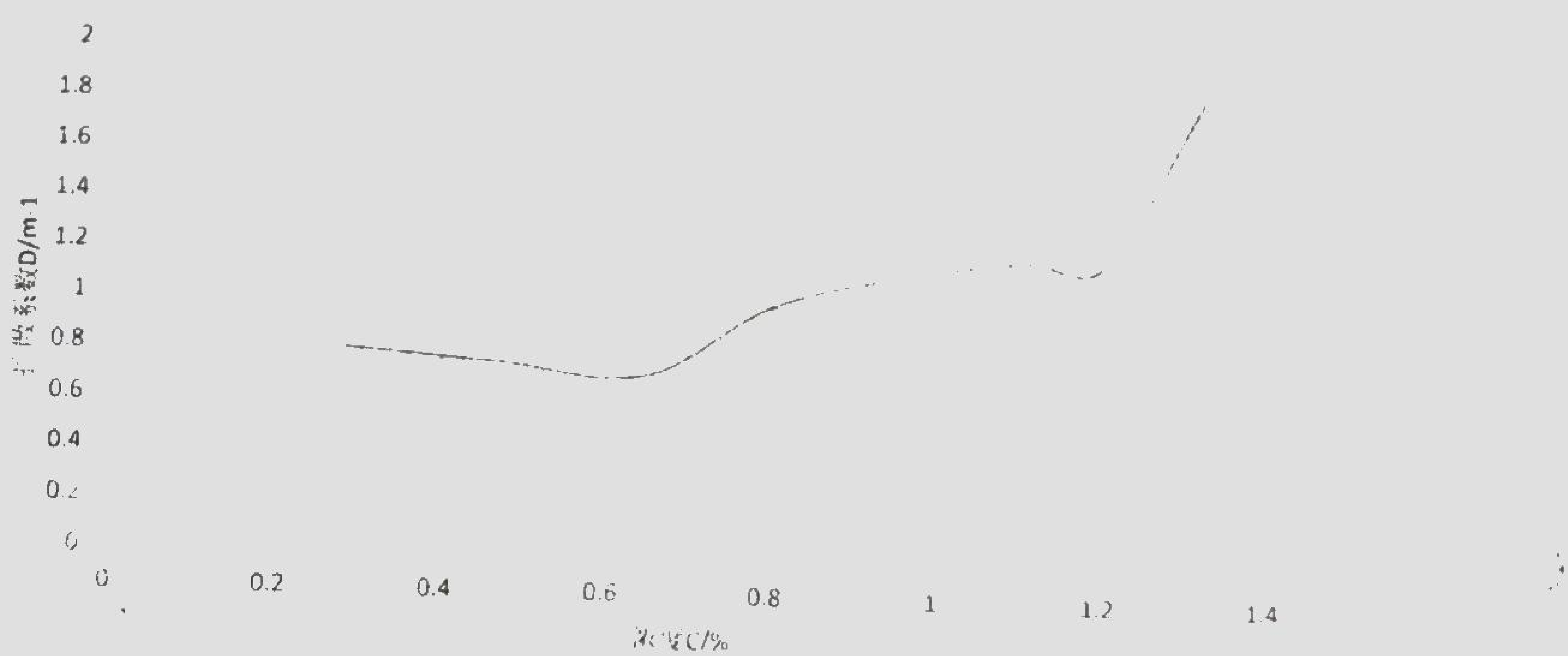
$= -D'(-10.8\ m^{-1})$

得 $D' = 1.0287\ g/(m\cdot h)$

$\therefore \text{Const} = D'\cdot\frac{dC}{d\rho} = -11.11g/(m^2\cdot h)$

同理计算得其它点处的 $D(C)$

Excel绘图如下：



8-6 边界条件: $t>0\left[\begin{array}{ll} x=\infty, & C_1=0.1\% \\ x=0, & C_0=1\% \end{array}\right.$

初始条件: $t=0$: $x>0$, $C=0.1\%$

将 C 全部下调 0.1%. $t>0\left[\begin{array}{ll} x=\infty & C_1=0 \\ x=0 & C_0=0.9\% \end{array}\right.$

$t=0$, $C=0$

(1) 由半无穷长系统扩散方程: $C=C_0[1-\mathrm{erf}(\beta)]$ $\beta=\frac{x}{2\sqrt{Dt}}$ $D=\cancel{5.4\times10^{-11}}$ 3.34×10^{-11} m^2/s

计算得: $\mathrm{erf}(\beta)=0.5$ $\beta=0.475$ $\therefore t=\frac{x^2}{4D\beta^2}=8293.75$

$\approx 2.3h$

(2) $x\to 2x$, β不变, 则 $t\to 4t$ 需要 $16587.4s$ 或者说 $4.61h$

(3) 设0.3% C 对应 β', 有 $\beta'=\frac{x_1}{2\sqrt{D_1t_1}}=\frac{x_2}{2\sqrt{D_2t_2}}$

$\frac{D_1}{D_2}=\exp\left(\frac{-140000}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)=2.085$

$\frac{t_1}{t_2}=1$ $\therefore \frac{x_1}{x_2}=\sqrt{\frac{D_1}{D_2}}=1.44$

8-7 边界条件 $t>0\left[\begin{array}{ll} x=\infty, & C_1=0.85\% \\ x=0, & C_0=0 \end{array}\right.$

初始条件: $t=0$ $x>0$, $C=0.85\%$

$\therefore C=C_1\,\mathrm{erf}(\beta)$ 当 $C=0.8\%$时: $\mathrm{erf}(\beta)=\frac{C}{C_1}=0.9412$ $\Rightarrow\beta=1.335$

$\beta=\frac{x}{2\sqrt{Dt}}$ 代入D, t 得 $x=2\sqrt{Dt}\cdot\beta=0.053cm$, 应车去 0.53mm

8-8. 迁移速度 $v=(D_{Cr}-D_{Fe})\frac{dN_{Cr}}{dx}=$ ~~1.52~~ $\cancel{cm/h}$ $\cancel{0.76\times10^{-3}}$ cm/h

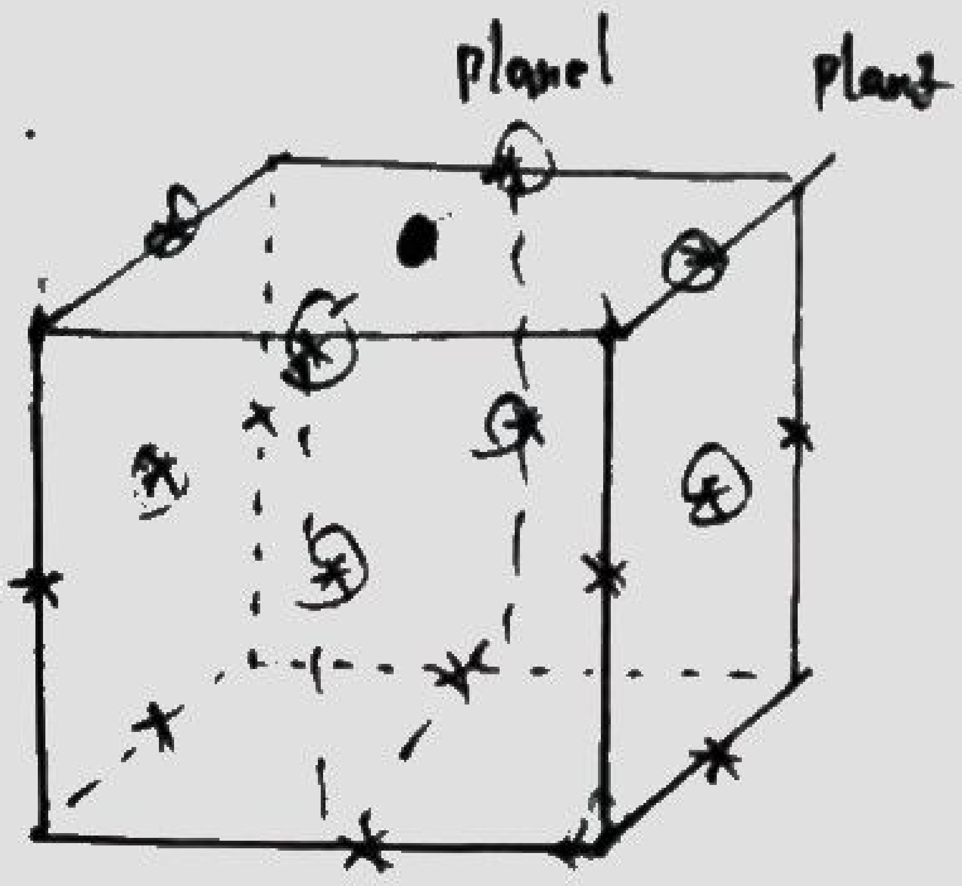
$\boxed{1:b\ \text{及}\Rightarrow b=\frac{l}{\sqrt{t}}\Rightarrow v=\frac{dl}{dt}=\frac{b}{2}\cdot t^{-\frac{1}{2}}=\frac{1}{2t}}$

Darken 公式: $D=N_{Fe}D_{Cr}+N_{Cr}D_{Fe}=1.43\times10^{-9}cm^2/s$

$N_{Cr}=0.478$, $N_{Fe}=0.522$ $\frac{dN_{Cr}}{dx}=126/cm$

得: $\left[\begin{array}{l} D_{Cr}-D_{Fe}=\cancel{1.21\times10^{-3}cm^2/h}\ \ 6.05\times10^{-6}cm^2/h \\ 0.522D_{Cr}+0.478D_{Fe}=\cancel{1.43\times10^{-9}}\ \ 5.148\times10^{-6}cm^2/h \end{array}\right.\Rightarrow\left]\begin{array}{l} D_{Cr}=7.657\times10^{-6}cm^2/h \\ D_{Fe}=1.607\times10^{-6}cm^2/h \end{array}\right.$

8-10.



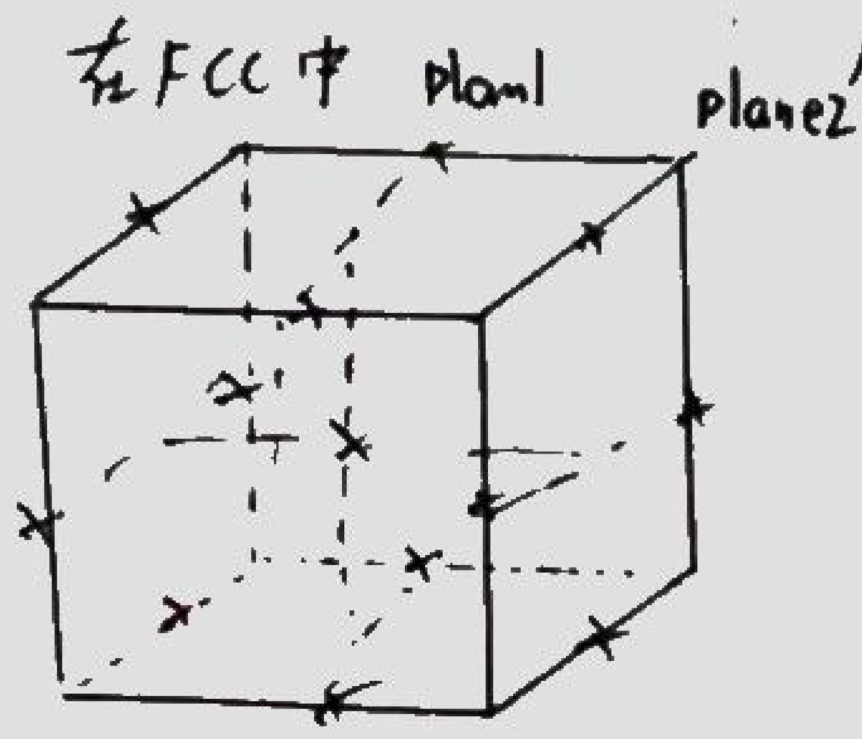
对于位于某一个八面体间隙中的C, 离它最近的八面体间隙本层(001)有4个, 上,下层$(00\frac{1}{2})$ $(00\frac{1}{2})$ 各有4个, 共12个

~~而离它最近的四面体间隙有4个~~

由Plane1 → Plane2 共有2个. $\therefore \alpha'=\frac{2}{12}=\frac{1}{6}$, $r=\frac{a}{2}$

$\therefore D=\alpha'\Gamma r^2=\frac{1}{6}\cdot\left(\frac{a}{2}\right)^2\cdot\Gamma=\frac{\Gamma a^2}{24}$

在FCC中



八面体间隙近邻原子共 $4+4+4=12$ 个. 到 Plane2 有4种方式. 机率为是$\frac{1}{3}$

$\therefore D=\alpha'\Gamma r^2=\frac{1}{3}\left(\frac{a}{2}\right)^2=\frac{\Gamma a^2}{12}$

8-14.(1) $D = D_0 \exp\left(-\frac{Q}{RT}\right)$

代入数据得: $\frac{D_1}{D_2} = \exp\left(-\frac{Q}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$

$$\frac{2\times10^{-13}}{4.75\times10^{-13}} = \exp\left(-\frac{Q}{8.3145\ J/mol}\cdot\left(\frac{1}{1009.15}-\frac{1}{1055.15}\right)\right)$$

得: $Q = 166.48\ kJ$ $\therefore D_0 = D_1\exp\left(\frac{Q}{RT_1}\right) = 8.28\times10^{-5}$

(2) 代入 $T_4 = 500°C + 273.15°C = 773.15\ K$ 得:

$$D_4 = D_0\exp\left(-\frac{Q}{RT_4}\right) = 4.69\times10^{-16}\ (m^2/s)$$

8-17.