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

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

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

∴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 $\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial x} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial x} = \frac{\partial f}{\partial \rho}\cos\varphi - \frac{\partial f}{\partial \varphi}\frac{\sin\varphi}{\rho}$

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

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

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,若假定了轴对称均匀扩散,则有 $\frac{\partial C}{\partial t} = \frac{\partial}{\partial \rho}\left(D\frac{\partial C}{\partial \rho}\right)$

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

ρ/cm	$w(C)$/%	$\frac{\partial C}{\partial \rho}/m^{-1}$	$D(C)$
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

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

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

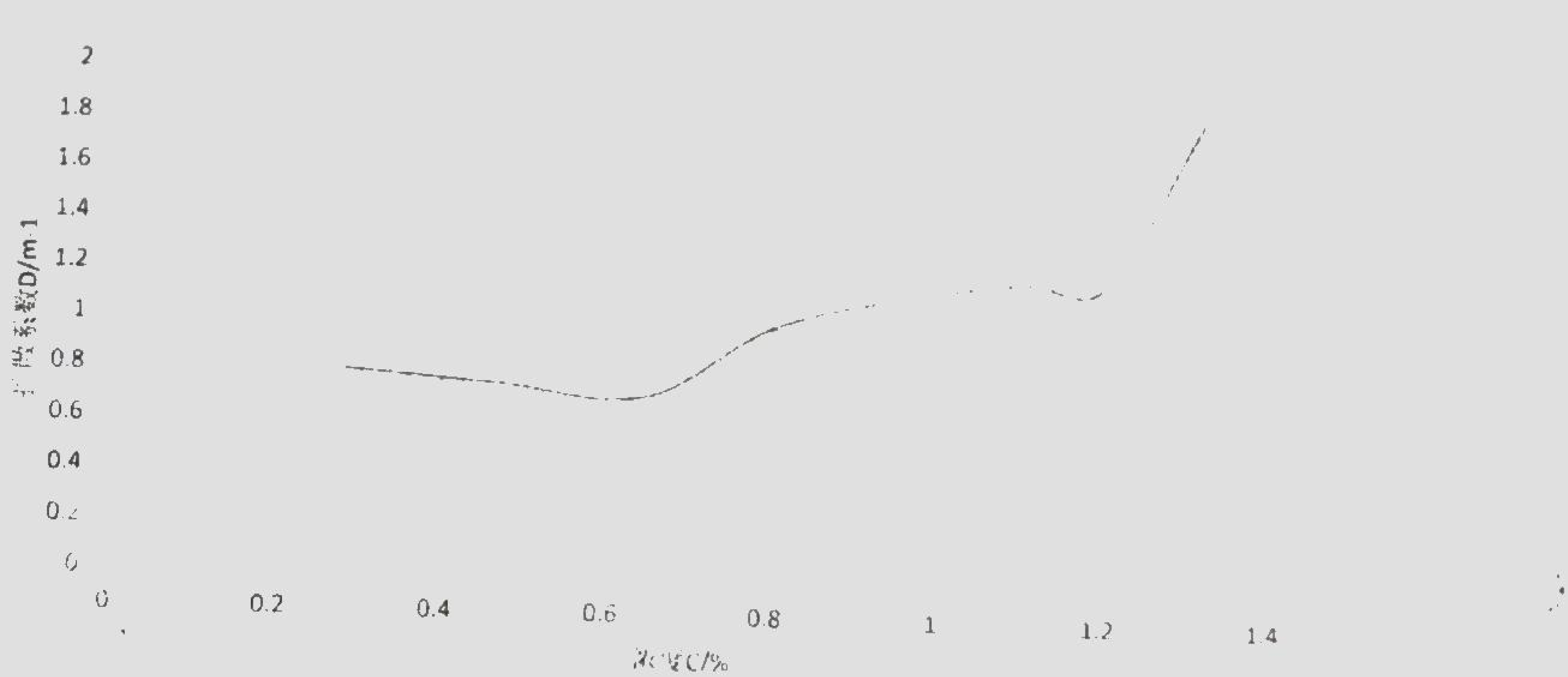
$= -D'(-10.8\ m^{-1})$

得 $D' = 1.0287\ g/(m\cdot h)$

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

同理可计算得其它点处的 $D(c)$

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: $C = C_0[1-\mathrm{erf}(\beta)]$ $\beta = \frac{x}{2\sqrt{Dt}}$ $D = \cancel{5.48\times10^{-15}}$ 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 4.61 h

(3) 设0.3% C 对应 β', 有 $\beta' = \frac{x_1}{2\sqrt{D_1 t_1}} = \frac{x_2}{2\sqrt{D_2 t_2}}$

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

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

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 0.53 mm

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

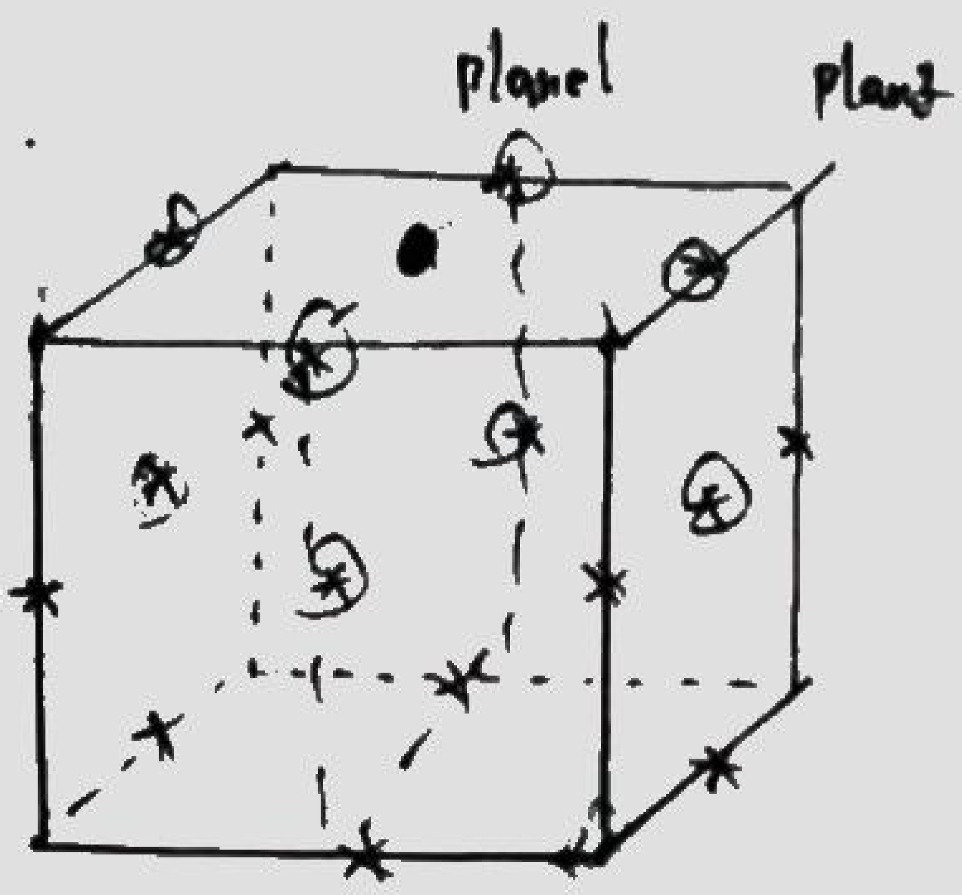
8-8. 迁移速度 $v = (D_{Cr} - D_{Fe})\frac{dN_{Cr}}{dx} = \cancel{1.52\times10^{-3}cm/h}$ 0.76×10^{-3} cm/h

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: $\left[\begin{array}{l} D_{Cr} - D_{Fe} = \cancel{1.21\times10^{-5}cm^2/h} \quad 6.05\times10^{-6}cm^2/h \\ 0.522D_{Cr} + 0.478D_{Fe} = 5.148\times10^{-6}cm^2/h \end{array} \right.$ $\Rightarrow \left[\begin{array}{l} D_{Cr} = 7.657\times10^{-6}cm^2/h \\ D_{Fe} = 1.607\times10^{-6}cm^2/h \end{array} \right.$

8-10.



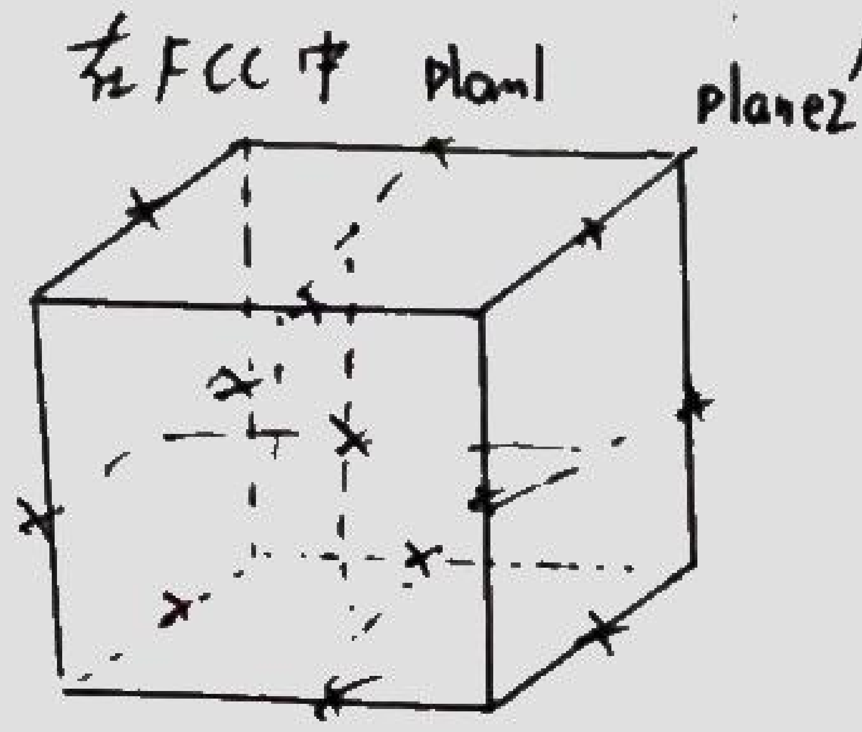
对于位于某一个八面体间隙中的C. 离它最近的八面体间隙本层(001)有4个, 上下层($00\frac{1}{2}$) ($00\frac{1}{2}$)各有4个. 共12个

~~而离它最近的四面体间隙有4个~~

由Plane 1 → 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$\frac{1}{3}$

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

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.