扩散方程

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第十四讲. 扩散方程

1. 质量传递微分方程
2. 通过静止气膜的扩散
3. 等分子反方向稳态扩散
4. 非定常分子扩散
5. 颗粒溶解

1. 质量传递微分方程

守恒原理的一般表达式

$$\boxed{\begin{matrix}\text{特征量}\\\text{变化速率}\end{matrix} = \begin{matrix}\text{特征量}\\\text{输入速率}\end{matrix} - \begin{matrix}\text{特征量}\\\text{输出速率}\end{matrix} + \begin{matrix}\text{特征量}\\\text{生成速率}\end{matrix}}$$

控制体内 A 质量
对时间的变化量

$$\frac{\partial M_A}{\partial t} = W_{A1} - W_{A2} + R_A$$

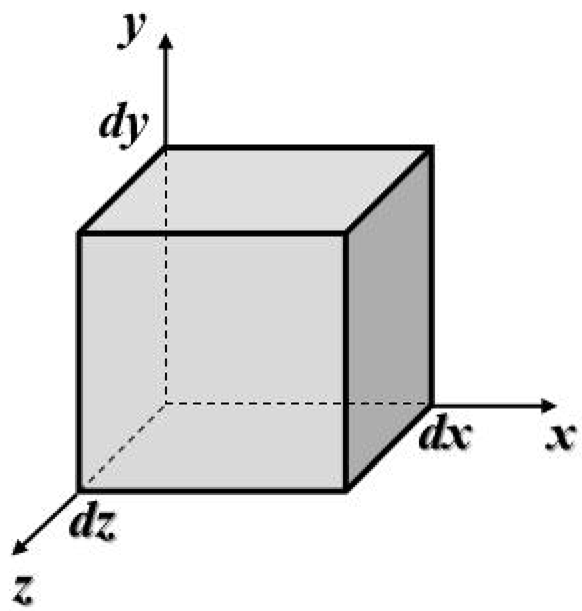
单位时间控制体内
因化学或物理过程
产生或消失的 A 质量

单位时间从控制面
输入和输出控制体的 A 质量

对流传质微分方程

控制体内 A 物质的质量变化速率：

$$\frac{\partial M_A}{\partial t} = \frac{\partial \rho_A}{\partial t} dxdydz$$



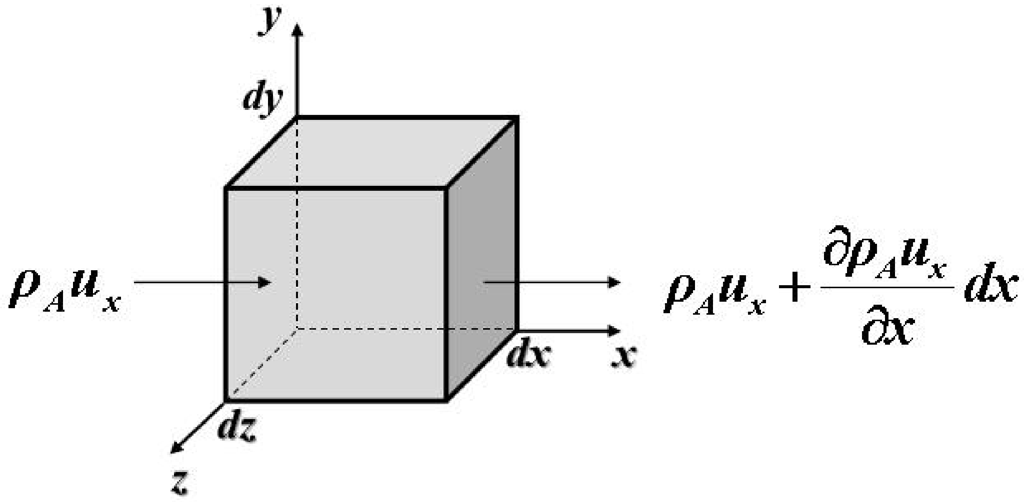
控制体内因化学反应产生或消失的A物质的质量，则其生成速率：

$$R_A = r_A dxdydz$$

其中 r_A 为单位体积控制体内 A 物质的质量生成速率。

质量输入和输出速率

流体流动带入和带出的质量净速率：



x 方向流动带入和带出的质量净速率：

$$\rho_A u_x dydz - \left(\rho_A u_x + \frac{\partial \rho_A u_x}{\partial x} dx \right) dydz = -\frac{\partial \rho_A u_x}{\partial x} dxdydz$$

同理　y 方向流动带入和带出的质量净速率：

$$\rho_A u_y dxdz - \left(\rho_A u_y + \frac{\partial \rho_A u_y}{\partial x} dy \right) dxdz = -\frac{\partial \rho_A u_y}{\partial y} dxdydz$$

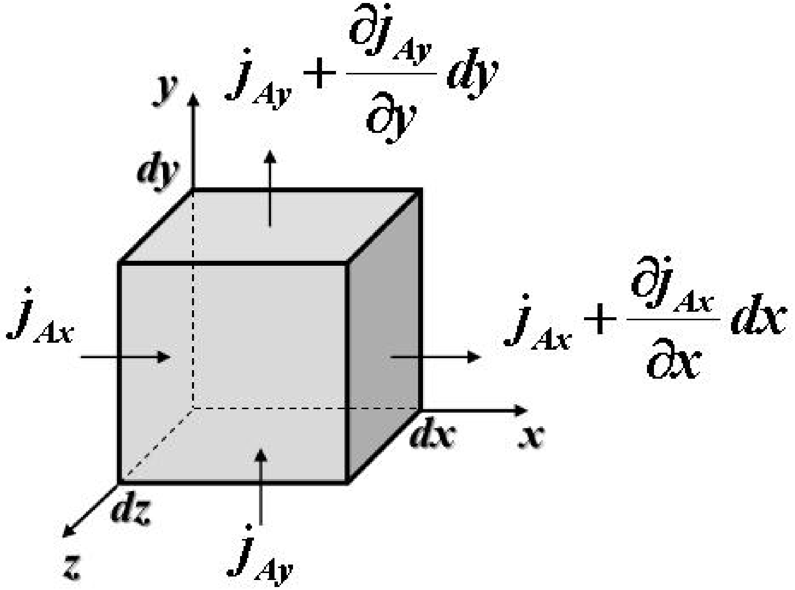
z 方向流动带入和带出的质量净速率：

$$\rho_A u_z dxdy - \left(\rho_A u_z + \frac{\partial \rho_A u_z}{\partial z} dz \right) dxdz = -\frac{\partial \rho_A u_z}{\partial z} dxdydz$$

流体流动带入和带出的总质量净速率：

$$-\left(\frac{\partial \rho_A u_x}{\partial x} + \frac{\partial \rho_A u_y}{\partial y} + \frac{\partial \rho_A u_z}{\partial z} \right) dxdydz$$

扩散产生的质量净速率：



x 方向扩散产生的质量净速率：

$$j_{Ax}dydz-\left(j_{Ax}+\frac{\partial j_{Ax}}{\partial x}dx\right)dydz=-\frac{\partial j_{Ax}}{\partial x}dxdydz$$

同理　　y 方向扩散产生的质量净速率：

$$j_{Ay}dxdz-\left(j_{Ay}+\frac{\partial j_{Ay}}{\partial y}dy\right)dxdz=-\frac{\partial j_{Ay}}{\partial y}dxdydz$$

z 方向扩散产生的质量净速率：

$$j_{Az}dxdy-\left(j_{Az}+\frac{\partial j_{Az}}{\partial z}dz\right)dxdy=-\frac{\partial j_{Az}}{\partial z}dxdydz$$

扩散产生的总质量净速率：

$$-\left(\frac{\partial j_{Ax}}{\partial x}+\frac{\partial j_{Ay}}{\partial y}+\frac{\partial j_{Az}}{\partial z}\right)dxdydz$$

质量输入和输出净速率：

$$W_{A1}-W_{A2}=-\left(\frac{\partial\rho_A u_x}{\partial x}+\frac{\partial\rho_A u_y}{\partial y}+\frac{\partial\rho_A u_z}{\partial z}\right)dxdydz-\left(\frac{\partial j_{Ax}}{\partial x}+\frac{\partial j_{Ay}}{\partial y}+\frac{\partial j_{Az}}{\partial z}\right)dxdydz$$

根据质量守恒 $$\frac{\partial M_A}{\partial t}=W_{A1}-W_{A2}+R_A$$

$$\frac{\partial\rho_A}{\partial t}=-\left(\frac{\partial\rho_A u_x}{\partial x}+\frac{\partial\rho_A u_y}{\partial y}+\frac{\partial\rho_A u_z}{\partial z}\right)-\left(\frac{\partial j_{Ax}}{\partial x}+\frac{\partial j_{Ay}}{\partial y}+\frac{\partial j_{Az}}{\partial z}\right)+r_A$$

$$\frac{\partial \rho_A}{\partial t} = -\left(\frac{\partial \rho_A u_x}{\partial x} + \frac{\partial \rho_A u_y}{\partial y} + \frac{\partial \rho_A u_z}{\partial z} \right) - \left(\frac{\partial j_{Ax}}{\partial x} + \frac{\partial j_{Ay}}{\partial y} + \frac{\partial j_{Az}}{\partial z} \right) + r_A$$

引入连续性方程： $$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0$$

费克分子扩散定律： $$j_{Ax} = -D_{AB} \frac{d\rho_A}{dx}$$

可得对流传质微分方程：

$$\frac{\partial \rho_A}{\partial t} + u_x \frac{\partial \rho_A}{\partial x} + u_y \frac{\partial \rho_A}{\partial y} + u_z \frac{\partial \rho_A}{\partial z} = D_{AB} \left(\frac{\partial^2 \rho_A}{\partial x^2} + \frac{\partial^2 \rho_A}{\partial y^2} + \frac{\partial^2 \rho_A}{\partial z^2} \right) + r_A$$

摩尔浓度 C_A 形式的对流传质微分方程：

$$\rho_A = M_A C_A$$

$$\frac{\partial C_A}{\partial t} + u_{Mx}\frac{\partial C_A}{\partial x} + u_{My}\frac{\partial C_A}{\partial y} + u_{Mz}\frac{\partial C_A}{\partial z} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right) + R_A$$

$$R_A = \frac{r_A}{M_A}$$

其中 R_A 为单位体积控制体内 A 物质的摩尔生成速率。

分子扩散微分方程

若A在静止介质B中扩散，可得分子扩散微分方程：

$$\frac{\partial \rho_A}{\partial t}=D_{AB}\left(\frac{\partial^2 \rho_A}{\partial x^2}+\frac{\partial^2 \rho_A}{\partial y^2}+\frac{\partial^2 \rho_A}{\partial z^2}\right)+r_A$$

无化学反应

$$\frac{\partial \rho_A}{\partial t}=D_{AB}\left(\frac{\partial^2 \rho_A}{\partial x^2}+\frac{\partial^2 \rho_A}{\partial y^2}+\frac{\partial^2 \rho_A}{\partial z^2}\right)$$

费克第二定律

定常

$$\frac{\partial^2 \rho_A}{\partial x^2}+\frac{\partial^2 \rho_A}{\partial y^2}+\frac{\partial^2 \rho_A}{\partial z^2}=-\frac{r_A}{D_{AB}}$$

定常且无化学反应

$$\frac{\partial^2 \rho_A}{\partial x^2}+\frac{\partial^2 \rho_A}{\partial y^2}+\frac{\partial^2 \rho_A}{\partial z^2}=0$$

拉普拉斯方程

摩尔浓度C_A形式的分子扩散微分方程：

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right) + R_A$$

无化学反应

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right)$$

定常

$$\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} = -\frac{R_A}{D_{AB}}$$

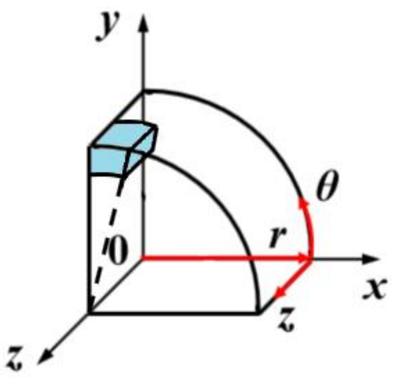
定常且无化学反应

$$\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} = 0$$

拉普拉斯方程

参考资料

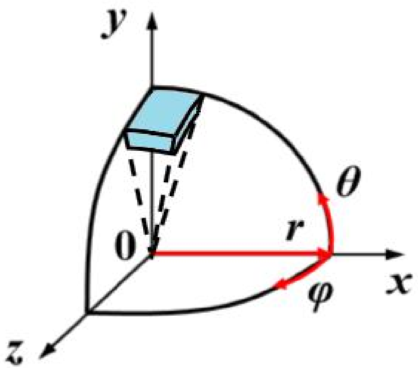
1.柱坐标系中的传质方程



$$\frac{\partial \rho_A}{\partial t}+u_r\frac{\partial \rho_A}{\partial r}+\frac{u_\theta}{r}\frac{\partial \rho_A}{\partial \theta}+u_z\frac{\partial \rho_A}{\partial z}=D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \rho_A}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2 \rho_A}{\partial \theta^2}+\frac{\partial^2 \rho_A}{\partial z^2}\right]+r_A$$

$$\frac{\partial C_A}{\partial t}+u_{Mr}\frac{\partial C_A}{\partial r}+\frac{u_{M\theta}}{r}\frac{\partial C_A}{\partial \theta}+u_{Mz}\frac{\partial C_A}{\partial z}=D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2 C_A}{\partial \theta^2}+\frac{\partial^2 C_A}{\partial z^2}\right]+R_A$$

2.球坐标系中的传质方程



$$\frac{\partial \rho_A}{\partial t}+u_r\frac{\partial \rho_A}{\partial r}+\frac{u_\theta}{r}\frac{\partial \rho_A}{\partial \theta}+\frac{u_\varphi}{r\sin\theta}\frac{\partial \rho_A}{\partial \varphi}$$

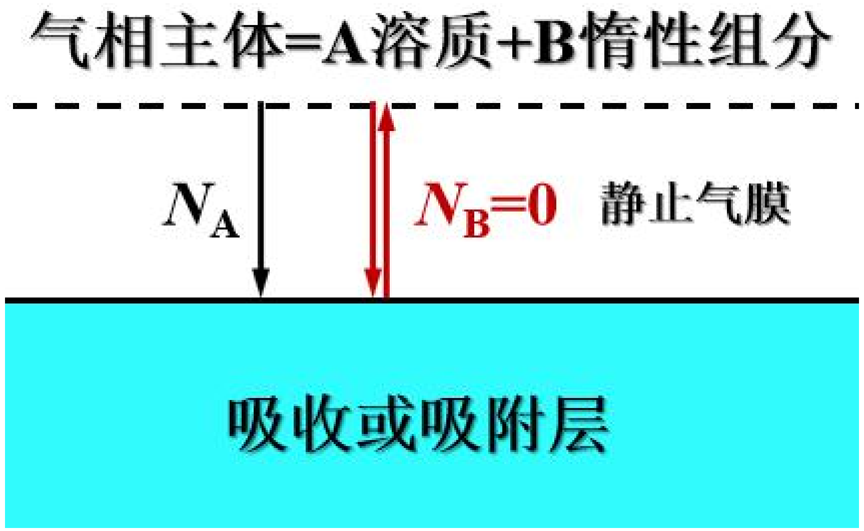
$$=D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \rho_A}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \rho_A}{\partial \theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 \rho_A}{\partial \varphi^2}\right]+r_A$$

$$\frac{\partial C_A}{\partial t}+u_{Mr}\frac{\partial C_A}{\partial r}+\frac{u_{M\theta}}{r}\frac{\partial C_A}{\partial \theta}+\frac{u_{M\varphi}}{r\sin\theta}\frac{\partial C_A}{\partial \varphi}$$

$$=D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial C_A}{\partial \theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 C_A}{\partial \varphi^2}\right]+R_A$$

2. 通过静止气膜的扩散

在气体吸收或吸附单元操作中，气体由溶质A和惰性组分B组成的二元混合物中，组分A通过静止组分B扩散至吸收表面被吸收。



$$\frac{\partial C_A}{\partial t}+u_{Mx}\frac{\partial C_A}{\partial x}+u_{My}\frac{\partial C_A}{\partial y}+u_{Mz}\frac{\partial C_A}{\partial z}=D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2}+\frac{\partial^2 C_A}{\partial y^2}+\frac{\partial^2 C_A}{\partial z^2}\right)+R_A$$

定常： $\dfrac{\partial C_A}{\partial t}=0$

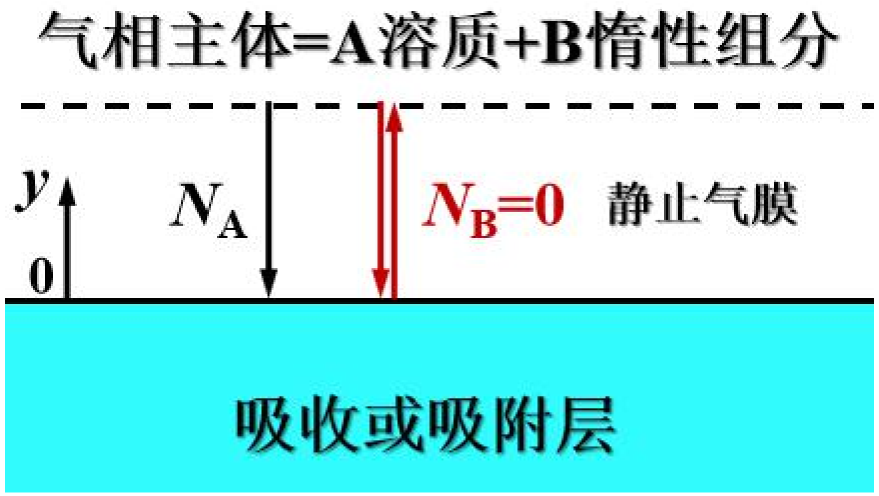
静止气膜中： $\begin{cases} u_{Mx}=0 \\ u_{My}\neq 0 \\ u_{Mz}=0 \end{cases}$ $\begin{cases} \dfrac{\partial C_A}{\partial x}=0 \\ \dfrac{\partial C_A}{\partial y}\neq 0 \\ \dfrac{\partial C_A}{\partial z}=0 \end{cases}$ $\begin{cases} \dfrac{\partial^2 C_A}{\partial x^2}=0 \\ \dfrac{\partial^2 C_A}{\partial y^2}\neq 0 \\ \dfrac{\partial^2 C_A}{\partial z^2}=0 \end{cases}$

无化学反应： $R_A=0$

简化对流传质微分方程得：

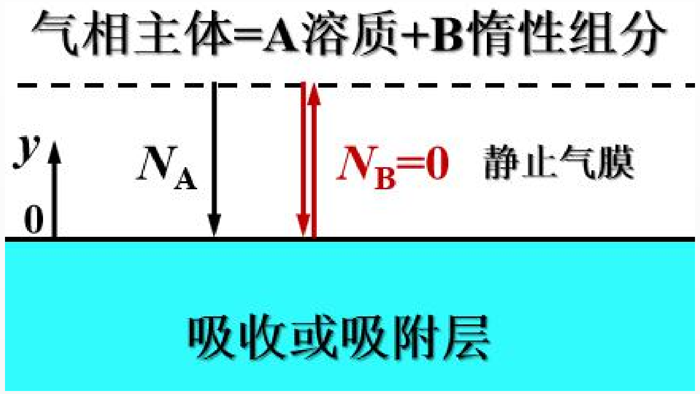
$$u_{My}\frac{\partial C_A}{\partial y}=D_{AB}\frac{\partial^2 C_A}{\partial y^2}$$

$$u_{My}\frac{\partial x_A}{\partial y}=D_{AB}\frac{\partial^2 x_A}{\partial y^2}$$



$$\because Cu_{My} = C_A u_{Ay} + C_B u_{By} = N_A + N_B = N_A$$

$$\therefore u_{My} = \frac{N_A}{C}$$



$$N_A \frac{dx_A}{dy} = CD_{AB} \frac{d^2 x_A}{dy^2}$$

积分:

$$\frac{N_A}{CD_{AB}} y = ln \frac{dx_A}{dy} + C_1$$

边界条件:

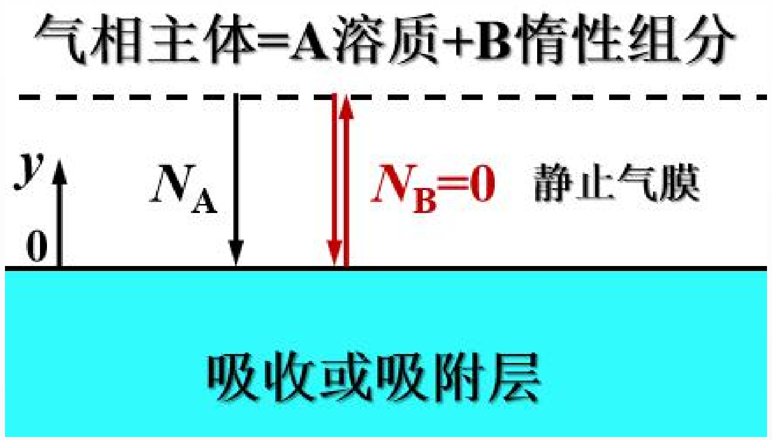
$$y = 0, \quad x_A = 0, \quad N_A = -CD_{AB} \left. \frac{dx_A}{dy} \right|_{y=0}$$

$$\therefore C_1 = -ln\left(-\frac{N_A}{CD_{AB}}\right)$$

得:

$$\frac{dx_A}{dy} = -\frac{N_A}{CD_{AB}} e^{\frac{N_A}{CD_{AB}} y}$$

$$\int_0^{x_A} dx_A = \int_0^{y} -\frac{N_A}{CD_{AB}} e^{\frac{N_A}{CD_{AB}}y} dy$$



$$x_A = 1 - e^{\frac{N_A}{CD_{AB}}y} \qquad N_A y = CD_{AB}\, ln(1 - x_A)$$

$$y = y_1 \quad x_A = x_{A1}; \quad N_A y_1 = CD_{AB}\, ln(1 - x_{A1})$$

$$y = y_2 \quad x_A = x_{A2}; \quad N_A y_2 = CD_{AB}\, ln(1 - x_{A2})$$

问题探讨

气膜中组分 B 静止吗?

$$N_A = \frac{CD_{AB}}{y - y_1} ln\frac{1 - x_A}{1 - x_{A1}} \qquad N_A = \frac{CD_{AB}}{y_2 - y_1} ln\frac{1 - x_{A2}}{1 - x_{A1}}$$

静止气膜中浓度分布： $$ln\frac{x_A - 1}{x_{A1} - 1} = \frac{y - y_1}{y_2 - y_1} ln\frac{x_{A2} - 1}{x_{A1} - 1}$$

$$\because x_A + x_B = 1 \qquad \therefore N_A = \frac{CD_{AB}}{y_2 - y_1} ln \frac{x_{B2}}{x_{B1}}$$

定义： $x_{B,ln} = \dfrac{x_{B2} - x_{B1}}{ln \dfrac{x_{B2}}{x_{B1}}}$

$$N_A = \frac{CD_{AB}}{x_{B,ln}} \frac{x_{B2} - x_{B1}}{y_2 - y_1} = \frac{CD_{AB}}{x_{B,ln}} \frac{x_{A1} - x_{A2}}{y_2 - y_1}$$

用对流传质模型表示：

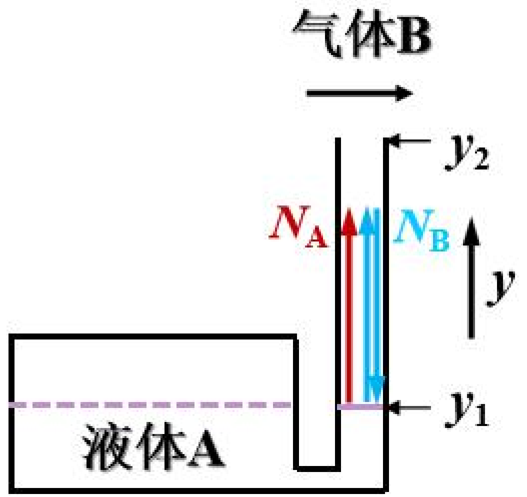
$$N_A = \frac{CD_{AB}}{(y_2 - y_1)x_{B,ln}}(x_{A1} - x_{A2}) = k_x(x_{A1} - x_{A2})$$

传质系数： $k_x = \dfrac{CD_{AB}}{(y_2 - y_1)x_{B,ln}}$

气体扩散系数测定

蒸发管测定气体扩散系数。组分A蒸发，通过静止组分B扩散至流体主流。B不溶于液体，过程定常，气体为理想气体。

解：　理想气体

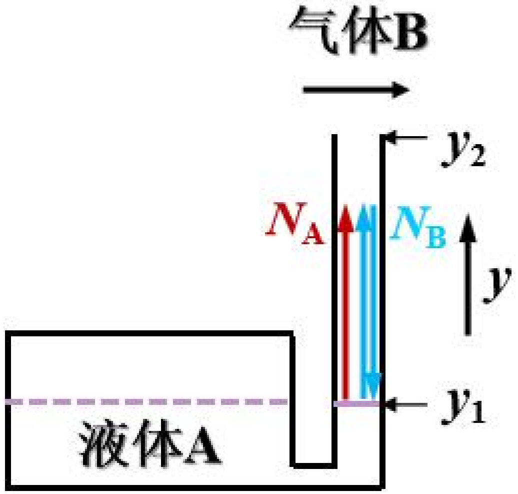


$$\frac{pV}{T}=nR \qquad C=\frac{n}{V}=\frac{p}{RT}$$

$$x_A=\frac{p_A}{p}$$

$$x_{B,ln}=\frac{p_{B2}-p_{B1}}{p\ln\frac{p_{B2}}{p_{B1}}}=\frac{p_{B,ln}}{p}$$

$$N_A = \frac{CD_{AB}}{x_{B,ln}} \frac{x_{A1} - x_{A2}}{y_2 - y_1} = \frac{pD_{AB}}{RTp_{B,ln}} \frac{p_{A1} - p_{A2}}{y_2 - y_1}$$

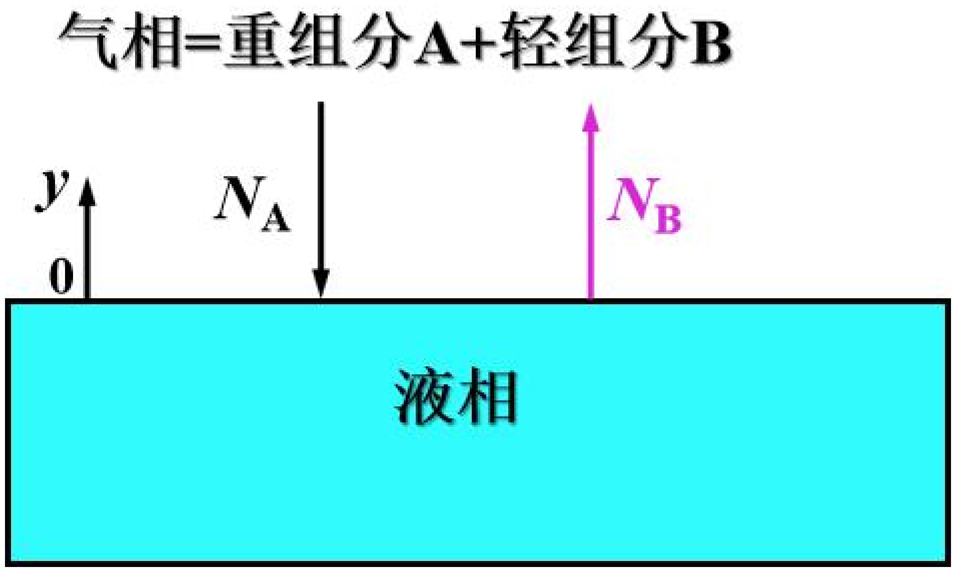


$$D_{AB} = \frac{N_A RTp_{B,ln}}{p} \frac{y_2 - y_1}{p_{A1} - p_{A2}}$$

组分 A 蒸发过程定常，N_A 由实验测得；
蒸发管中 $y = y_1$， $p = p_{A1}$，p_{A1}为 p、T 下组分A的饱和蒸气压；
$y = y_2$， $p = p_{A2} \approx 0$，组分A扩散到管口处，立即被大量气体B带走，故 $p_{A2} \approx 0$。

3. 等分子反方向稳态扩散

在蒸馏和精馏单元操作中，组分 A、B 进行反方向扩散，若二者扩散的通量相等，则称为等分子反方向扩散。



$$\because Cu_{My} = C_A u_{Ay} + C_B u_{By} = N_A + N_B = N_A - N_A = 0$$

$$\therefore u_{My} = 0$$

定常： $\dfrac{\partial C_A}{\partial t} = 0$

静止气膜中： $\begin{cases} u_{Mx} = 0 \\ u_{My} = 0 \\ u_{Mz} = 0 \end{cases}$ $\begin{cases} \dfrac{\partial C_A}{\partial x} = 0 \\ \dfrac{\partial C_A}{\partial y} \neq 0 \\ \dfrac{\partial C_A}{\partial z} = 0 \end{cases}$ $\begin{cases} \dfrac{\partial^2 C_A}{\partial x^2} = 0 \\ \dfrac{\partial^2 C_A}{\partial y^2} \neq 0 \\ \dfrac{\partial^2 C_A}{\partial z^2} = 0 \end{cases}$

无化学反应： $R_A = 0$

简化对流传质微分方程得：

$$\frac{\partial^2 C_A}{\partial y^2} = 0$$

$$\frac{d^2C_A}{dy^2}=0 \qquad C_A=C_1y+C_2$$

边界条件：

$$\begin{cases} y=y_1, \ C_A=C_{A1} \\ y=y_2, \ C_A=C_{A2} \end{cases} \qquad \begin{cases} C_1=\dfrac{C_{A1}-C_{A2}}{y_1-y_2} \\ C_2=C_{A1}-\dfrac{C_{A1}-C_{A2}}{y_1-y_2}y_1 \end{cases}$$

液相表面上气膜中浓度分布：

$$\frac{C_A-C_{A1}}{C_{A1}-C_{A2}}=\frac{y-y_1}{y_1-y_2}$$

传质通量：

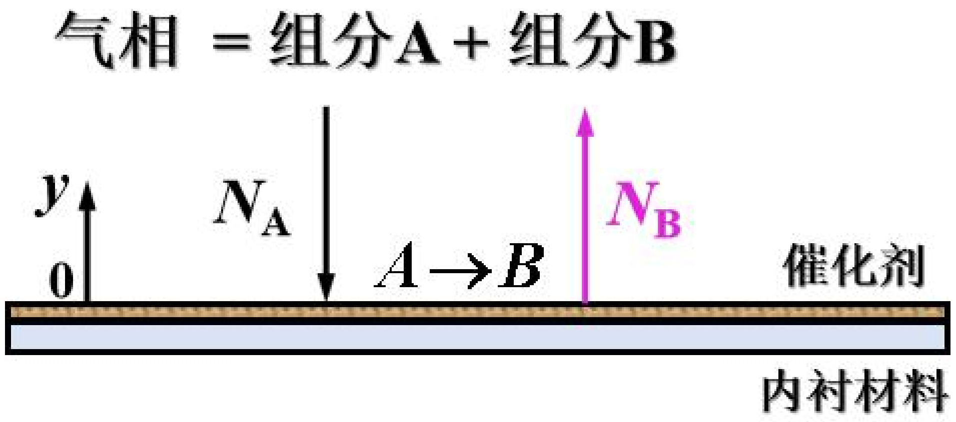
$$N_{Ax}=J_{Ax}+x_A\left(N_{Ax}+N_{Bx}\right)=J_{Ax}=-D_{AB}\frac{dC_A}{dy}$$

课后思考

1.伴有化学反应的扩散过程

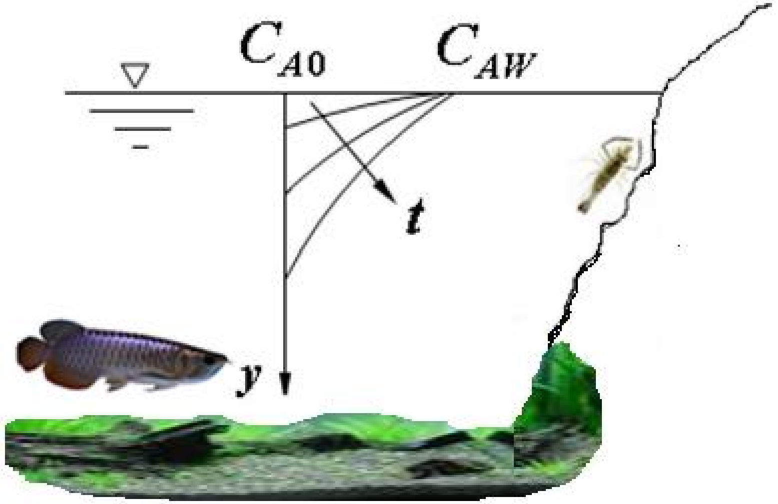
（1）若反应速率大大高于扩散速率，扩散决定传质速率，称为扩散控制过程；

（2）若反应速率远远低于扩散速率，化学反应决定传质速率，称为反应控制过程。



4. 非定常分子扩散

冰冻的湖面融化，水中的氧含量随时间，沿深度变化。



将湖水简化为半无限大平壁，氧扩散为非定常分子扩散。

分子扩散微分方程：

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right) + R_A$$

相似的问题，相似的解：

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{\partial^2 C_A}{\partial y^2}$$

解方程得浓度分布：

$$\frac{C_A - C_{AW}}{C_{A0} - C_{AW}} = \frac{2}{\sqrt{\pi}} \int_0^{\eta} e^{-\eta^2} d\eta = erf\left(\eta\right)$$

式中： $\eta = \dfrac{y}{\sqrt{4D_{AB}t}}$

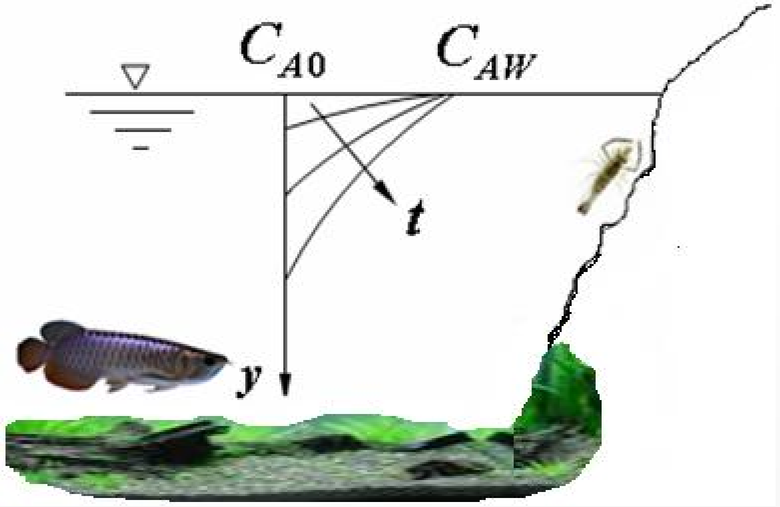
***t* 时刻水面处的氧扩散通量：**

$$N_{At,y=0} = -D_{AB} \left.\frac{\partial C_A}{\partial y}\right|_{y=0} = -D_{AB} \left.\left(\frac{\partial C_A}{\partial \eta} \frac{\partial \eta}{\partial y}\right)\right|_{y=0} = \sqrt{\frac{D_{AB}}{\pi t}}\left(C_{AW} - C_{A0}\right)$$

0~*t* 时间内通过单位面积水面的氧扩散量：

$$N_A = \int_0^t N_{At,y=0} dt = \int_0^t \sqrt{\frac{D_{AB}}{\pi t}}\left(C_{AW} - C_{A0}\right) dt = 2\sqrt{\frac{D_{AB} t}{\pi}}\left(C_{AW} - C_{A0}\right)$$

湖水中含氧量变化



已知：$C_{A0} = 3.0\times10^{-5}$ kmol/m^3，
$C_{AW} = 3.06\times10^{-4}$ kmol/m^3，
$D_{AB} = 1.58\times10^{-9}$ m^2/s。

求：三天后，离湖面0.06m深处的氧浓度。

解：
$$\eta = \frac{y}{\sqrt{4D_{AB}t}} = \frac{0.06}{\sqrt{4\times1.58\times10^{-9}\times3\times24\times3600}} = 1.48$$

查误差函数表，线性内插得：
$$\frac{C_A - C_{AW}}{C_{A0} - C_{AW}} = erf(\eta) = 0.9633$$

氧浓度为：
$$C_A = 4.01\times10^{-5}\text{kmol/m}^3$$

课后思考

1.对比静止流体中的平板启动、半无限大平壁非定常导热和湖水中含氧量变化。体会传递现象的类似性。

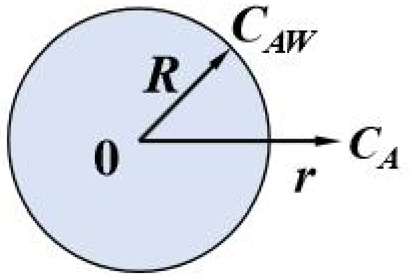
$$\frac{u_x - U_W}{U_0 - U_W} = erf(\eta) \qquad \eta = \frac{y}{\sqrt{4\nu t}}$$

$$\frac{T - T_W}{T_0 - T_W} = erf(\eta) \qquad \eta = \frac{y}{\sqrt{4at}}$$

$$\frac{C_A - C_{AW}}{C_{A0} - C_{AW}} = erf(\eta) \qquad \eta = \frac{y}{\sqrt{4D_{AB}t}}$$

5. 颗粒溶解

球形颗粒中含有微量的可溶物质A，向周围静止的液相中扩散。假定颗粒表面为饱和浓度 C_{AW}，且维持不变，液相主体浓度为 0，传质过程定常。



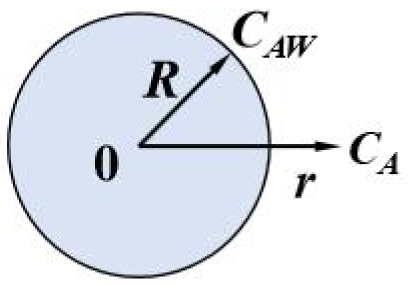
球坐标系

$$\frac{\partial C_A}{\partial t}+u_{Mr}\frac{\partial C_A}{\partial r}+\frac{u_{M\theta}}{r}\frac{\partial C_A}{\partial \theta}+\frac{u_{M\varphi}}{r\sin\theta}\frac{\partial C_A}{\partial \varphi}$$

$$=D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial C_A}{\partial \theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 C_A}{\partial \varphi^2}\right]+R_A$$

简化得： $$0=D_{AB}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)$$

$$\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right)=0$$



边界条件： $\begin{cases} r=R, & C_A=C_{AW} \\ r\to\infty, & C_A=0 \end{cases}$

颗粒表面液相中浓度分布： $\dfrac{C_A}{C_{AW}}=\dfrac{R}{r}$

物质A的溶解速率：

$$W=J_{Ar}\Big|_{r=R}4\pi R^2=-D_{AB}\frac{dC_A}{dr}\Big|_{r=R}4\pi R^2=\frac{D_{AB}C_{AW}}{R}$$

课后思考

1.缓释药片、缓释化肥和农药有何优点。如何控制其缓释速率。