4.八个重要的关系式

$$T=\left(\frac{\partial U}{\partial S}\right)_V=\left(\frac{\partial H}{\partial S}\right)_p \qquad S=-\left(\frac{\partial A}{\partial T}\right)_V=-\left(\frac{\partial G}{\partial T}\right)_p$$

$$p=-\left(\frac{\partial U}{\partial V}\right)_S=-\left(\frac{\partial A}{\partial V}\right)_T \qquad V=\left(\frac{\partial \mathrm{H}}{\partial p}\right)_S=\left(\frac{\partial G}{\partial p}\right)_T$$

$$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V \qquad \mathrm{d}H=T\mathrm{d}S+V\mathrm{d}p$$

$$\mathrm{d}A=-S\mathrm{d}T-\mathrm{p}\mathrm{d}V \qquad \mathrm{d}G=-S\mathrm{d}T+V\mathrm{d}p$$

4. 麦克斯韦关系式

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad \left(\frac{\partial^2 Z}{\partial x \partial y}\right) = \left(\frac{\partial^2 Z}{\partial y \partial x}\right)$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \Longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \Longrightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V \Longrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \Longrightarrow -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

5.热力学函数关系式的推导和证明

例1 对于恒容过程

$$dS = \frac{\delta Q_r}{T} = \frac{dU_V}{T} = \frac{C_V dT}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

例2 $U = f(T,V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\therefore\ dU = C_V dT + \left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\}dV$$

同理

$$dH = C_p dT + \left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\}dp$$

S随p或V的变化关系：

例3

$$-\left(\frac{\partial S}{\partial p}\right)_T=\left(\frac{\partial V}{\partial T}\right)_p$$

定义等压膨胀系数 $\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

代入上式积分得： $\Delta S=-\int_{p_1}^{p_2}\alpha V dp$

$$\because pV=nRT \quad \because \quad \alpha V=\left(\frac{\partial V}{\partial T}\right)_p=\frac{nR}{p}$$

$$\Delta S=-\int_{p_1}^{p_2}\alpha V dp=-\int_{p_1}^{p_2}\frac{nR}{p}dp=nR\,ln\frac{p_1}{p_2}=nR\,ln\frac{V_2}{V_1}$$

§ 3.9 克拉佩龙方程 (Clapeyronequation)

1.Clapeyron方程

T,p

$T \rightarrow T+\mathrm{d}T$

$p \rightarrow p+\mathrm{d}p$

$$\begin{tikzcd}
B(\alpha) \arrow[r, shift left, "\text{平衡}"] & B(\beta) \arrow[l, shift left] \\
G_{\mathrm{m}}(\alpha) \arrow[d] & G_{\mathrm{m}}(\beta) \arrow[d] \\
B(\alpha) \arrow[r, shift left, "\text{平衡}"] & B(\beta) \arrow[l, shift left] \\
G_{\mathrm{m}}(\alpha)+\mathrm{d}G_{\mathrm{m}}(\alpha) & G_{\mathrm{m}}(\beta)+\mathrm{d}G_{\mathrm{m}}(\beta)
\end{tikzcd}$$

$$G_{\mathrm{m}}(\alpha)=G_{\mathrm{m}}(\beta)$$

$$G_{\mathrm{m}}(\alpha)+\mathrm{d}G_{\mathrm{m}}(\alpha)=G_{\mathrm{m}}(\beta)+\mathrm{d}G_{\mathrm{m}}(\beta)$$

$$\boxed{\mathrm{d}G_{\mathrm{m}}(\alpha)=\mathrm{d}G_{\mathrm{m}}(\beta)}$$

$$\mathrm{d}G_\mathrm{m}(\alpha) = \mathrm{d}G_\mathrm{m}(\beta)$$

$$\mathrm{d}G_\mathrm{m}(\alpha) = -S_\mathrm{m}(\alpha)\mathrm{d}T + V_\mathrm{m}(\alpha)\mathrm{d}p$$

$$\mathrm{d}G_\mathrm{m}(\beta) = -S_\mathrm{m}(\beta)\mathrm{d}T + V_\mathrm{m}(\beta)\mathrm{d}p$$

$$-S_\mathrm{m}(\alpha)\mathrm{d}T + V_\mathrm{m}(\alpha)\mathrm{d}p = -S_\mathrm{m}(\beta)\mathrm{d}T + V_\mathrm{m}(\beta)\mathrm{d}p$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_\mathrm{m}(\beta) - S_\mathrm{m}(\alpha)}{V_\mathrm{m}(\beta) - V_\mathrm{m}(\alpha)} = \frac{\Delta_{\text{相变}}S_\mathrm{m}}{\Delta_{\text{相变}}V_\mathrm{m}} = \frac{\Delta_{\text{相变}}H_\mathrm{m}}{T\Delta_{\text{相变}}V_\mathrm{m}}$$

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{相变}}H_\mathrm{m}}{T\Delta_{\text{相变}}V_\mathrm{m}}}$$

2.Clausius-Clapeyron方程

将Clapeyron方程用于气—液及气—固平衡

$$\Delta V_m = V_m(g) - V_m(l) \approx V_m(g) = \frac{RT}{p}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H_{\mathrm{m}}}{T V_{\mathrm{m}}(\mathrm{g})} = \frac{\Delta_{\mathrm{vap}} H_{\mathrm{m}} p}{R T^2}$$

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H_{\mathrm{m}}}{R T^2}$$

$$\ln\left[\frac{p}{Pa}\right] = -\frac{\Delta_{\mathrm{vap}} H_{\mathrm{m}}}{RT} + C$$

$$ln\frac{p_2}{p_1} = -\frac{\Delta_{\mathrm{vap}} H_{\mathrm{m}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

*克—克方程的应用条件：

1. 因$\Delta V_m \approx V_g$, 在靠近临界点时不能用。

2. $V_m(g)=RT/p$适用于理想气体，高压下不能用。

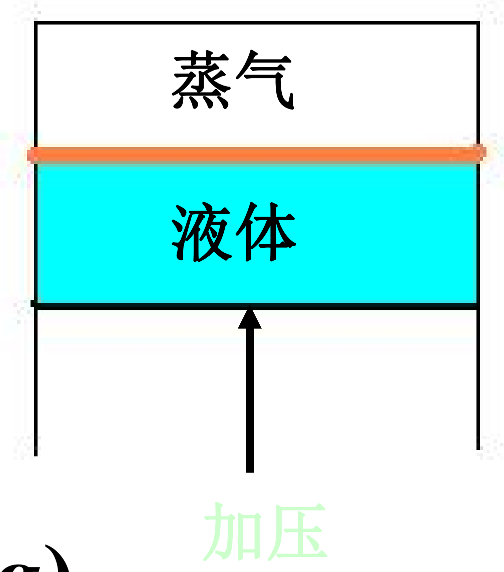
3. 因将ΔH_m当常数，只有在温度变化不大时才适用。

安托万(Antoine)方程是对克—克方程最简单的改进

$$\ln\left[\frac{p}{Pa}\right]=A-\frac{B}{T/K+C}$$

3. 外压对液体蒸气压的影响

$$G_m(l) = G_m(g)$$



恒温下液体压力改变 $dp(l)$,

蒸气压力改变 $dp(g)$,引起 G_m 变化

$dG_m(l)$ 及 $dG_m(g)$

$$G_m(l) + dG_m(l) = G_m(g) + dG_m(g)$$

即 $dG_m(l) = dG_m(g)$

恒温下 $dG_m = -SdT + Vdp = Vdp$

则 $V_m(l)dp(l) = V_m(g)dp(g)$

$$\boxed{\frac{dp(g)}{dp(l)} = \frac{V_m(l)}{V_m(g)}}$$

$$\boxed{\frac{dp(g)}{dp(l)} = \frac{V_m(l)}{V_m(g)}}$$

若蒸气为理想气体

$$\begin{cases} V_m(g) = \dfrac{RT}{p(g)} \\ \dfrac{d\ln p(g)}{dp(l)} = \dfrac{V_m(l)}{RT} \end{cases}$$

$$\ln\frac{p_2(g)}{p_1(g)} = \frac{V_m(l)}{RT}[p_2(l) - p_1(l)]$$

例 酚的精制采取减压蒸馏方法。已知酚的正常沸点为181.9℃，如真空度为86.7kPa，酚的沸点应为多少？已知酚的蒸发焓为 $48.1\times10^{3}\,\mathrm{J\cdot mol^{-1}}$ ，外压为100.0kPa。

解：

$$T_1,\ p_1 \xrightarrow{\Delta H} T_2,\ p_2$$

$$p_1^* = 101.3\mathrm{kPa} \qquad T_1 = (181.9 + 273.2)\mathrm{K} = 455.1\mathrm{K}$$

$$p_2^* = (100.0 - 86.7)\mathrm{kPa} = 13.3\mathrm{kPa}$$

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}} = 48.1\times10^{3}\,\mathrm{J\cdot mol^{-1}} \Longrightarrow T_2 = ?$$

$$\ln\left(\frac{13.3}{101.3}\right) = -\frac{48.1\times10^{3}}{8.3145}\left(\frac{1}{T_2/\mathrm{K}} - \frac{1}{455.1}\right)$$

$T_2 = 392.4\mathrm{K} \rightarrow 119.2$℃

例：已知纯A液体在360K的饱和蒸气压为81.06kPa,在此条件下,A(l)的摩尔气化热 $\Delta_{vap}H_m=40kJ\cdot mol^{-1}$.

$C_{p,m}(l)=75kJ\cdot mol^{-1}K^{-1}$

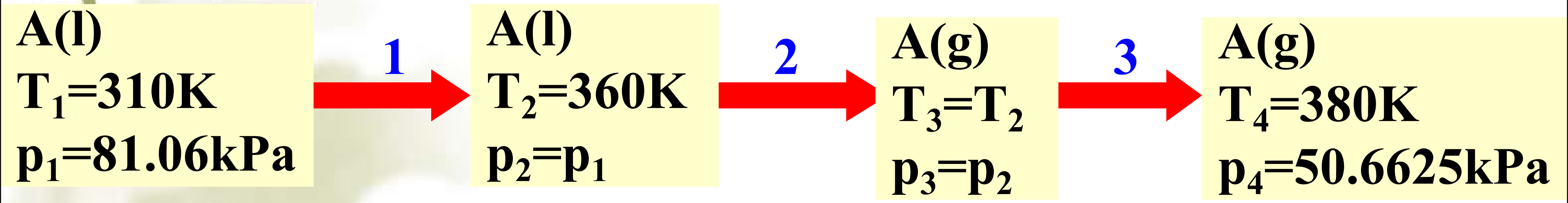
$C_{p,m}(g)=(30+10^{-2}T/K)J\cdot mol^{-1}K^{-1}$

$S_m^{\theta}(g,380K)=174.35J\cdot K^{-1}\cdot mol^{-1}$

假定A(*g*)为理想气体,忽略温度的变化对A(*l*)体积的影响.试计算下列始、末状态之间的ΔU_m、ΔH_m、ΔS_m、ΔG_m及ΔA_m

$A(l,\ 310K,\ 81.06kPa)\rightarrow A(g,\ 380K,\ 50.6625kPa)$

解：



A(l)
$T_1=310K$
$p_1=81.06kPa$

1

A(l)
$T_2=360K$
$p_2=p_1$

2

A(g)
$T_3=T_2$
$p_3=p_2$

3

A(g)
$T_4=380K$
$p_4=50.6625kPa$

$$\Delta H_1=C_{p,m}(l)(T_2-T_1)=[75\times(360-310)]J\cdot mol^{-1}=3750\ J\cdot mol^{-1}$$

$$\Delta H_2=\Delta_{vap}H_m=40kJ\cdot mol^{-1}$$

$$\Delta H_3=\int_{T_3}^{T_4}C_{p,m}(g)dT=\int_{263K}^{380K}(30+10^{-2}T/K)J\cdot mol^{-1}dT=674J\cdot mol^{-1}$$

$$\Delta H_m=\Delta H_1+\Delta H_2+\Delta H_3=44.42kJ\cdot mol^{-1}$$

$$\Delta(pV)=p_4V_4-p_1V_1\approx p_4V_4=nRT_4=3.159\times10^3\ J\cdot mol^{-1}$$

$$\Delta U=\Delta H-\Delta(pV)=41.265kJ\cdot mol^{-1}$$

$$\Delta S_1=C_{p,m}(l)\ln(T_2/T_1)=11.215\ J\cdot mol^{-1}K^{-1}$$

$$\Delta S_2=\Delta_{vap}H_m/T_2=111.111\ J\cdot mol^{-1}K^{-1}$$

$$\Delta S_3 = \int_{T_3}^{T_4} \frac{C_{p,m}}{T} dT + R\ln\frac{p_3}{p_4}$$

$$= \left[30\ln\frac{T_4}{T_3} + 10^{-2}\left(T_4 - T_3\right) + R\ln\frac{p_3}{p_4}\right] J\cdot mol^{-1}\cdot K^{-1}$$

$$= 5.730 J\cdot mol^{-1}\cdot K^{-1}$$

$\Delta S_m = \Delta S_1 + \Delta S_2 + \Delta S_3 = 128.06 \mathrm{J\cdot mol^{-1}K^{-1}}$

$S_4 = S_m^{\theta}(g, 380K) + \Delta S(p^{\theta} \rightarrow p_4)$

$= S_m^{\theta}(g, 380K) + R\ln(p^{\theta}/p_4) = 180.00 \mathrm{J\cdot mol^{-1}K^{-1}}$

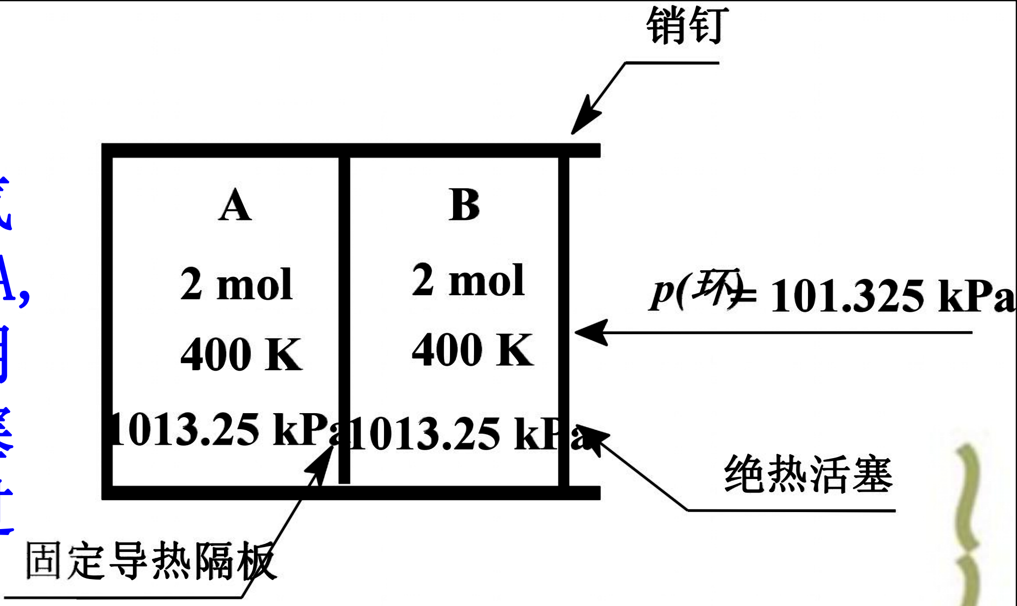
$S_1 = S_4 - \Delta S_m = 51.91 \mathrm{J\cdot mol^{-1}K^{-1}}$

$\Delta(TS_m) = T_4S_4 - T_1S_1 = 52.299 \mathrm{J\cdot mol^{-1}}$

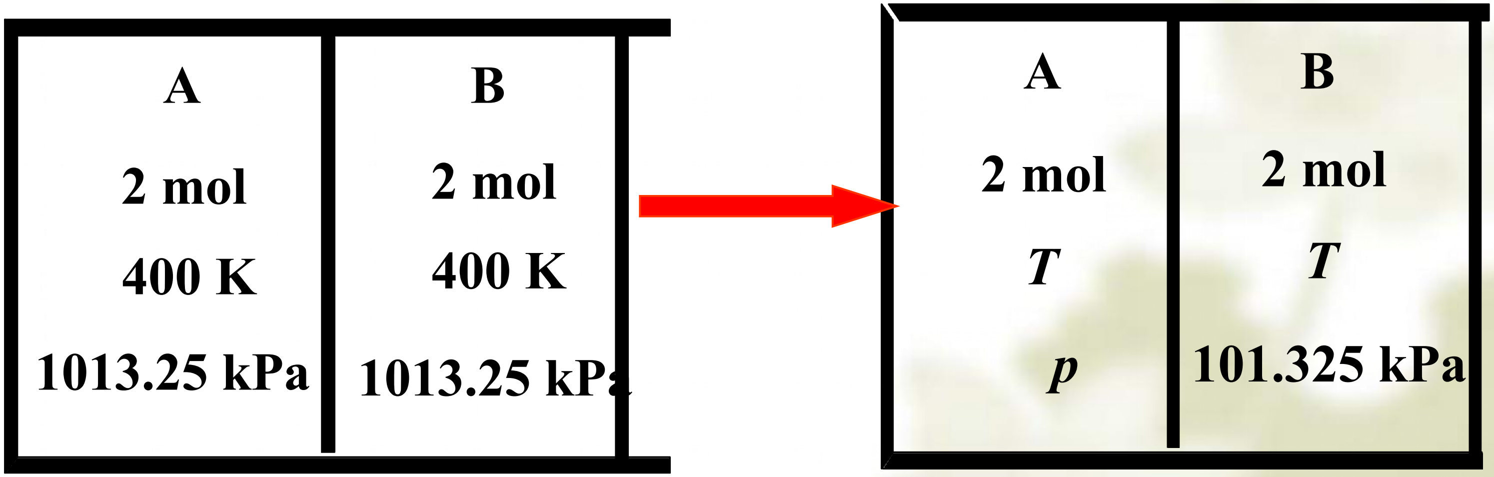
$\Delta G_m = \Delta H_m - \Delta(TS_m) = -7.875 \mathrm{kJ\cdot mol^{-1}}$

$\Delta A_m = \Delta U_m - \Delta(TS_m) = -11.034 \mathrm{kJ\cdot mol^{-1}}$

如图所示，一带活塞（无质量，绝热）的绝热汽缸中放有一固定导热良好刚性隔板，此隔板将气缸分成左，右两室并分别放入 A, B 两种理想气体。开始时活塞用销钉固定，当销钉去掉后，活塞移动。当系统达平衡时，求此过程的 W、ΔH 和 ΔS。A(g)与B(g)的 $C_{v,m}$= 3R/2。



解:



分析：（1）过程绝热。（2）A 气体体积不变。

（3）A 气体和 B 气体处于热平衡。

$$\Delta U = \Delta U_A + \Delta U_B = Q + W = W$$

$$n_A C_{V,m}(A)\cdot(T-400K) + n_B C_{V,m}(B)\cdot(T-400K) = -p_{ex}\left(\frac{n_B RT}{p_{ex}} - \frac{n_B RT_1}{p_1}\right)$$

$$6R(T-400K) = -2RT + 80R \qquad \Rightarrow T = 310\,(\mathrm{K})$$

$$W = \Delta U = 6R(T-400K) = 6\times 8.314\times(310-400)J = -4489.56\ J$$

$$\Delta H = \Delta H_A + \Delta H_B = nC_{p,m}\Delta T = 4\times\frac{5}{2}R(310K-400K) = -7482.6\ (\mathrm{J})$$

$$\Delta S = \Delta S_A + \Delta S_B = n_A C_{V,m}\, ln\frac{T_2}{T_1} + \left(n_B C_{p,m}\, ln\frac{T_2}{T_1} + n_B R\, ln\frac{p_1}{p_2}\right)$$

$$= n_B(C_{V,m} + C_{p,m})\, ln\frac{T_2}{T_1} + n_B R\, ln\frac{p_1}{p_2}$$

$$= \left(8\times 8.314\, ln\frac{310}{400} + 2\times 8.314\, ln\frac{1013.25}{101.325}\right)J = 21.33\ (J\cdot K^{-1})$$

第四章 多组分系统热力学

Chapter 4 the Thermodynamics of Multicomponent System

系统按照所含组分数和相数可划分为：

单组分均相系统	多组分均相系统
单组分多相系统	多组分多相系统

多组分均相系统 ——由两种或两种以上物质以分子状态相互混合而成的均匀系统

多组分均相系统按照处理方法的不同分为：

混合物 ***mixture*** 系统中各组分以相同的标准和方法加以研究的均相系统

溶 液 ***solution*** 系统中各组分以不同的标准和方法加以研究，分为**溶剂**（***solvent***）和**溶质**（***solute***），

- 多组分均相系统
  - 混合物
    - 理想
    - 非理想
      - 气
      - 液
      - 固
  - 溶液
    - 理想
    - 非理想
      - 液
        - 电解质
        - 非电解质
      - 固