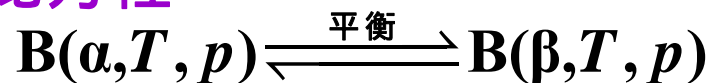


§ 3.8 热力学第二定律在单组分系统相平衡中的应用

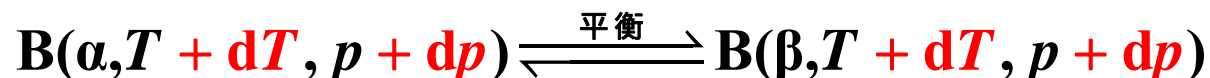
1. 克拉佩龙方程

根据吉布斯函数判据式



$$G_m(\alpha) = G_m(\beta)$$

$$dG_{T,p} \leq 0 \begin{cases} < \text{自发} \\ = \text{平衡} \end{cases}$$



$$G_m(\alpha) + dG_m(\alpha) = G_m(\beta) + dG_m(\beta)$$

将基本方程式用于每一相 $dG_m(\alpha) = -S_m(\alpha)dT + V_m(\alpha)dp$

$$dG_m(\beta) = -S_m(\beta)dT + V_m(\beta)dp$$

$$\because dG_m(\alpha) = dG_m(\beta) \quad \therefore -S_m(\alpha)dT + V_m(\alpha)dp = -S_m(\beta)dT + V_m(\beta)dp$$

$$\Delta_\alpha^\beta S_m = S_m(\beta) - S_m(\alpha)$$

$$\Delta_\alpha^\beta V_m = V_m(\beta) - V_m(\alpha)$$

$$\Delta_\alpha^\beta S_m dT = \Delta_\alpha^\beta V_m dp$$

$$\text{得} \quad \frac{dp}{dT} = \frac{\Delta_\alpha^\beta S_m}{\Delta_\alpha^\beta V_m} \quad \text{或} \quad \frac{dT}{dp} = \frac{\Delta_\alpha^\beta V_m}{\Delta_\alpha^\beta S_m}$$



1. 克拉佩龙方程

$$\Delta_{\alpha}^{\beta} S_m = S_m(\beta) - S_m(\alpha) \quad \Delta_{\alpha}^{\beta} S_m dT = \Delta_{\alpha}^{\beta} V_m dp \quad \text{得} \quad \frac{dp}{dT} = \frac{\Delta_{\alpha}^{\beta} S_m}{\Delta_{\alpha}^{\beta} V_m} \quad \text{或} \quad \frac{dT}{dp} = \frac{\Delta_{\alpha}^{\beta} V_m}{\Delta_{\alpha}^{\beta} S_m}$$
$$\Delta_{\alpha}^{\beta} V_m = V_m(\beta) - V_m(\alpha)$$

$$\because \Delta_{\alpha}^{\beta} S_m = \frac{\Delta_{\alpha}^{\beta} H_m}{T} \quad \therefore \frac{dp}{dT} = \frac{\Delta_{\alpha}^{\beta} H_m}{T \Delta_{\alpha}^{\beta} V_m}$$

称克拉佩龙方程，表示纯物质两相平衡时压力与温度变化的函数关系

讨论：在蒸发、升华过程中，平衡压力 p 即为温度为 T 时的饱和蒸汽压。

熔化、晶型转变过程克拉佩龙方程常改写为

$$\frac{dT}{T} = \frac{\Delta_s^l V_m}{\Delta_s^l H_m} dp$$

近似认为 $\Delta_s^l V_m, \Delta_s^l H_m$ 与温度、压力无关，

$$\ln \frac{T_2}{T_1} = \frac{\Delta_s^l V_m}{\Delta_s^l H_m} (p_2 - p_1)$$



4.47 汞Hg在100 kPa下的熔点为-38.87 ，此时比熔化焓

$\Delta_{\text{fus}}h=9.75\text{J/g}$ ；液态汞和固态汞的密度分别为 $\rho(\text{l})=13.690\text{g}\cdot\text{cm}^{-3}$
 $\rho(\text{s})=14.193\text{g}\cdot\text{cm}^{-3}$

求：(1) 压力为10MPa下汞的熔点；

(2) 若要汞的熔点为-35 ，压力需增大多少。

解(1) 据克拉佩龙方程，外压与熔点的关系为 $\ln \frac{T_2}{T_1} = \frac{\Delta_s^1 V_m}{\Delta_s^1 H_m} (p_2 - p_1)$

$$\Delta_s^1 H_m = M(\text{Hg}) \cdot \Delta_{\text{fus}} h \quad \because \rho = \frac{m}{V} = \frac{m/M}{V/M} = \frac{n}{V/M} = \frac{M}{V/n} = \frac{M}{V_m} \quad \therefore V_m = \frac{M}{\rho}$$

$$\begin{aligned} \Delta_s^1 V_m &= V_m(\text{l}) - V_m(\text{s}) = M(\text{Hg}) \left(\frac{1}{\rho(\text{l})} - \frac{1}{\rho(\text{s})} \right) = M(\text{Hg}) \left(\frac{1}{13.690} - \frac{1}{14.193} \right) \times 10^{-6} \text{m}^3 \cdot \text{g}^{-1} \\ &= M(\text{Hg}) \times 2.589 \times 10^{-9} \text{m}^3 \cdot \text{g}^{-1} \end{aligned}$$

$$\ln \frac{T_2}{T_1} = \frac{[1/\rho(\text{l}) - 1/\rho(\text{s})]}{\Delta_{\text{fus}} h} (p_2 - p_1) = \frac{(1/13.690 - 1/14.193) \times 10^{-6}}{9.75} (10^7 - 100 \times 10^3)$$

$$T_2 = (1.0027 \times 234.28) \text{K} = 234.91 \text{K}$$

$$(2) \quad p = p_1 + \frac{\Delta_s^1 H_m}{\Delta_s^1 V_m} \ln \frac{T}{T_1} = \left(100 \times 10^3 + \frac{9.75}{2.589 \times 10^{-9}} \ln \frac{238.15}{234.28} \right) \text{Pa} = 61.8 \text{MPa}$$

2. 克劳修斯-克拉佩龙方程(液-气、固-气平衡的蒸气压方程)

若达蒸发平衡 $\frac{dp}{dT} = \frac{\Delta_1^g H_m}{T \Delta_1^g V_m}$

讨论: (1) $\Delta_1^g H_m > 0$, $\Delta_1^g V_m = V_m(g) - V_m(l) > 0$

故 $dp / dT > 0$ 表明温度升高, 液体的饱和蒸气压增大。

(2) 在远低于临界温度下, $\Delta_1^g V_m = V_m(g) - V_m(l) \approx V_m(g)$

若饱和蒸气近似满足理想气体状态方程, $V_m(g) = RT / p$ 得

$$\frac{dp}{dT} = \frac{p \Delta_1^g H_m}{RT^2} \quad \text{即} \quad \frac{dp}{p} = \frac{\Delta_1^g H_m}{RT^2} dT \quad \text{克-克方程的微分式}$$

(3) 若在两不同温度间 $\Delta_1^g H_m$ 可视为定值

定积分 $\ln \frac{p_2}{p_1} = -\frac{\Delta_1^g H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ 不定积分: $\ln p = -\frac{\Delta_1^g H_m}{RT} + C$

适用于液-气、固-气两相平衡

2. 克劳修斯-克拉佩龙方程(液-气、固-气平衡的蒸气压方程)

例：液态的磷在不同温度下的饱和蒸气压见下表：

T/K	349.8	401.2
p/Pa	133.3	1333

- (1) 计算液态磷的标准摩尔气化焓；
- (2) 已知三相点的温度为317.3 K，计算这时的饱和蒸气压；

解：(1) 由克-克方程 $\ln \frac{p(T_2)}{p(T_1)} = \frac{\Delta_{\text{vap}} H_{\text{m}}^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ 得

$$\Delta_{\text{vap}} H_{\text{m}}^{\ominus} = 52.27 \text{ kJ} \cdot \text{mol}^{-1}$$

(2) 由于三相点的温度为317.3 K时，根据克-克方程得，

$$\ln \frac{p_2}{133.3 \text{ Pa}} = \frac{52.27 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \left(\frac{1}{349.8 \text{ K}} - \frac{1}{317.3 \text{ K}} \right) \quad p_2 = 21.20 \text{ Pa}$$

