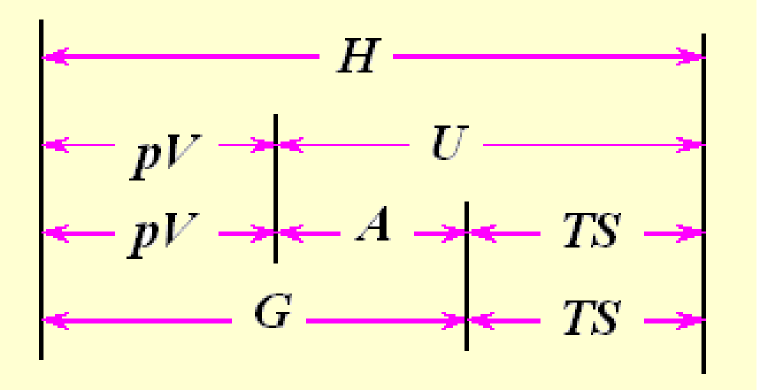
§ 3.7　热力学基本方程及麦克斯韦关系式

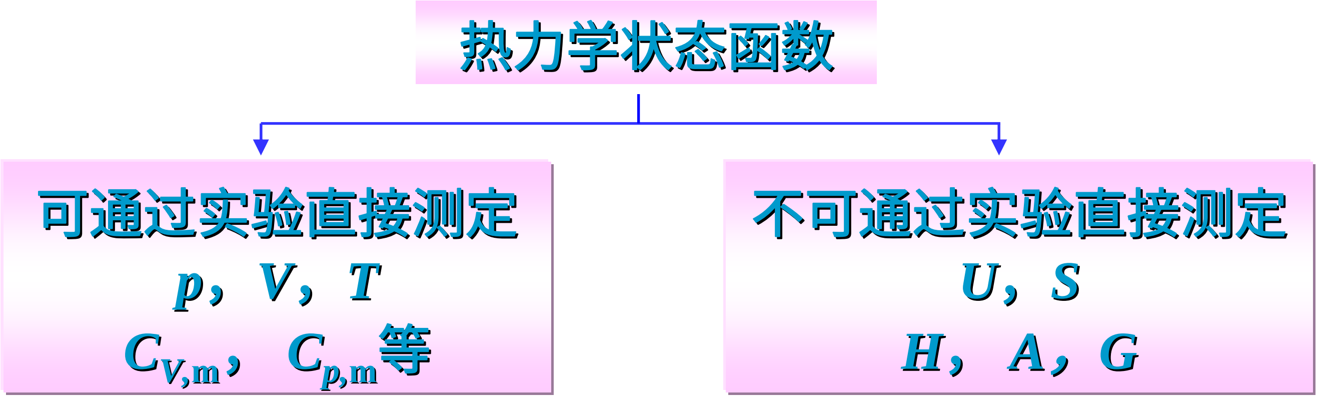
◎ U, S →第一、二定律基本函数

◎ H, A, G →组合辅助函数

◎ U, H →能量恒算

◎ S, A, G →判断过程的方向与限度





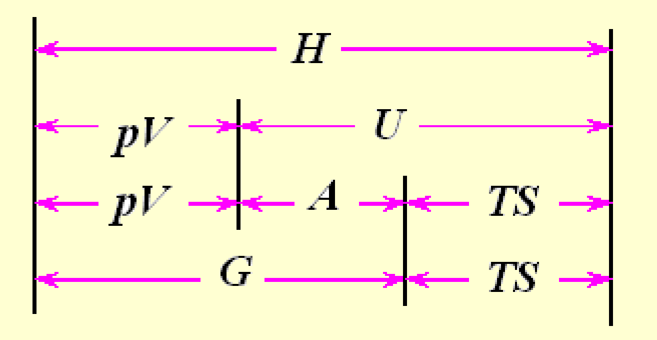
热力学状态函数

可通过实验直接测定
p，V，T
$C_{V,\mathrm{m}}$，$C_{p,\mathrm{m}}$等

不可通过实验直接测定
U，S
H，A，G

找出可测变量与不可直接测定的函数间的关系

1. 热力学基本方程



（1） 热力学函数的基本关系式

$H=U+pV$，$A=U-TS$，$G=H-TS$

（2） 基本方程

设系统经微小的可逆过程从平衡态1变到邻近的平衡态2，
据热一律 $\mathrm{d}U=\delta Q_r - p\mathrm{d}V$

据热二律 $\mathrm{d}S=\dfrac{\delta Q_r}{T}$ 得联合公式 $\boxed{\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V}$

$$\begin{tikzcd}
\boxed{\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V} \arrow[r, "\substack{H=U+pV \\ \mathrm{d}H=\mathrm{d}U+p\mathrm{d}V+V\mathrm{d}p}"] \arrow[d, "\substack{A=U-TS \\ \mathrm{d}A=\mathrm{d}U-T\mathrm{d}S-S\mathrm{d}T}"'] & \boxed{\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p} \arrow[d, "\substack{G=H-TS \\ \mathrm{d}G=\mathrm{d}H-T\mathrm{d}S-S\mathrm{d}T}"] \\
\boxed{\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V} & \boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p}
\end{tikzcd}$$

称为热力学基本方程

（适用条件：封闭系统、可逆过程、$W'=0$）

1.　热力学基本方程

(3)由热力学基本方程计算纯物质pVT变化过程的ΔA，ΔG

$$\boxed{\begin{aligned} \mathrm{d}A &= -S\mathrm{d}T - p\mathrm{d}V \\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}p \end{aligned}} \quad \text{恒温时} \quad \boxed{\begin{aligned} \mathrm{d}A &= -p\mathrm{d}V \\ \mathrm{d}G &= V\mathrm{d}p \end{aligned}}$$

※ 理想气体，将$pV = nRT$代入，积分得

$$\Delta A_T = -\int_{V_1}^{V_2} p\mathrm{d}V = -nRT\ln\frac{V_2}{V_1} = \Delta G_T = \int_{p_1}^{p_2} V\mathrm{d}p = nRT\ln\frac{p_2}{p_1}$$

※ 凝聚态物质，体积可认为不变

$$\Delta A_T = -\int_{V_1}^{V_2} p\mathrm{d}V \approx 0 \qquad \Delta G_T = \int_{p_1}^{p_2} V\mathrm{d}p = V\Delta p \xrightarrow{\text{压力变化不大}} \Delta G_T \approx 0$$

◀

※ 恒温下凝聚态间的化学反应，摩尔反应吉布斯函数变随压力的变化为

$$\boxed{\mathrm{d}\Delta_\mathrm{r}G_\mathrm{m} = \Delta_\mathrm{r}V_\mathrm{m}\mathrm{d}p} \qquad \boxed{\Delta_\mathrm{r}G_{\mathrm{m}_2} - \Delta_\mathrm{r}G_{\mathrm{m}_1} = \int_{p_1}^{p_2} \Delta V\mathrm{d}p}$$

2、*U*，*H*，*A*，*G* 的一阶偏导数关系式

（1）一阶偏导数关系式

由四个热力学基本方程，分别加上相应的条件，则

$$\boxed{\begin{aligned} dU &= TdS - pdV \\ dH &= TdS + Vdp \\ dA &= -SdT - pdV \\ dG &= -SdT + Vdp \end{aligned}}$$

$$\left\{ \begin{array}{ll} \left(\frac{\partial U}{\partial S}\right)_V = T; & \left(\frac{\partial U}{\partial V}\right)_S = -p \\ \left(\frac{\partial H}{\partial S}\right)_p = T; & \left(\frac{\partial H}{\partial p}\right)_S = V \\ \left(\frac{\partial A}{\partial T}\right)_V = -S; & \left(\frac{\partial A}{\partial V}\right)_T = -p \\ \underline{\left(\frac{\partial G}{\partial T}\right)_p} = -S; & \left(\frac{\partial G}{\partial p}\right)_T = V \end{array} \right\}$$

偏导数关系式

- ●由一阶偏导数关系式可推导出某状态函数在一个独立变量不变时随另一独立变量的变化率。
- ●通过等式右边变量的符号，可判断变化率的符号。

如，因*S*>0，随着温度*T*的升高，系统的*G*一定减小。

2、U，H，A，G 的一阶偏导数关系式

（2）吉布斯—亥姆霍兹方程

最常用的是 $\left(\dfrac{\partial G}{\partial T}\right)_p = -S$ 和 $\left(\dfrac{\partial A}{\partial T}\right)_V = -S$

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{TS+G}{T^2} = -\frac{H}{T^2}$$

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{T^2} = -\frac{S}{T} - \frac{A}{T^2} = -\frac{TS+A}{T^2} = -\frac{U}{T^2}$$

$$\underbrace{\boxed{\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}} \quad \boxed{\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T^2}}} \Rightarrow$$

表示G/T 在恒压下随T 的变化及A/T 在恒容下随T的变化。

吉布斯—亥姆霍兹方程

对于化学反应，可得到相应公式

$$\boxed{\frac{\mathrm{d}\left(\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\ominus}/T\right)}{\mathrm{d}T} = -\frac{\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\ominus}}{T^2}}$$

3．麦克斯韦关系式

若 z 为 x、y 的连续函数，$z = f(x, y)$，其全微分为：

$$\boxed{dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy} \qquad dz = Mdx + Ndy \qquad M = \left(\frac{\partial z}{\partial x}\right)_y, N = \left(\frac{\partial z}{\partial y}\right)_x$$

$$\because \left\{\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right\}_x = \left\{\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right\}_y \qquad \therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\left.\begin{array}{ll} \text{由 } dU = TdS - pdV\text{，得} & (\partial T/\partial V)_S = -(\partial p/\partial S)_V \\ \text{由 } dH = TdS + Vdp\text{，得} & (\partial T/\partial p)_S = (\partial V/\partial S)_p \\ \text{由 } dA = -SdT - pdV\text{，得} & \underline{(\partial S/\partial V)_T = (\partial p/\partial T)_V} \\ \text{由 } dG = -SdT + Vdp\text{，得} & \underline{-(\partial S/\partial p)_T = (\partial V/\partial T)_p} \end{array}\right\} \text{麦克斯韦关系式}$$

每个麦克斯韦关系式表示系统在同一状态的两种变化率数值相等。

意义：将不易由实验直接测定的热力学函数偏微商与易由实验直接测定的p、V、T的偏微商联系起来，使热力学函数关系式可由实验直接测定。

4．其它重要的热力学关系式

(1) $\left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{nC_{V,\mathrm{m}}}{T}$ 与 $\left(\dfrac{\partial S}{\partial T}\right)_p = \dfrac{nC_{p,\mathrm{m}}}{T}$

恒容可逆 $\delta Q_V = T\mathrm{d}S = nC_{V,\ \mathrm{m}}\mathrm{d}T$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{nC_{V,\mathrm{m}}}{T}$$

恒压可逆 $\delta Q_p = T\mathrm{d}S = nC_{p,\ \mathrm{m}}\mathrm{d}T$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{nC_{p,\mathrm{m}}}{T}$$

(2) 循环公式

对纯物质和组成不变的单相系统 ,只有两个独立变量 $z=f\,(x,y)$，其全微分：

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y \xrightarrow{z\text{ 恒定时，}\mathrm{d}z=0} \left(\frac{\partial z}{\partial x}\right)_y \cdot \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x$$

整理上式得 $\boxed{\left(\dfrac{\partial z}{\partial x}\right)_y \cdot \left(\dfrac{\partial x}{\partial y}\right)_z \cdot \left(\dfrac{\partial y}{\partial z}\right)_x = -1}$ 循环公式

z、x、y三个变量顺序求偏导的积为–1

例如$U=f\,(S,V)$ $\left(\dfrac{\partial U}{\partial S}\right)_V \cdot \left(\dfrac{\partial S}{\partial V}\right)_U \cdot \left(\dfrac{\partial V}{\partial U}\right)_S = -1$

5．热力学函数关系式应用

（1）计算

例3.7.1 已知25°C时液体汞Hg(l)的体膨胀系数 $\alpha_V = 1.82\times10^{-4}\,\mathrm{K}^{-1}$ 密度 $\rho = 13.534\times10^{3}\ \mathrm{kg\cdot m^{-3}}$。设外压改变时液体汞的体积不变求在25°C、压力从100 kPa增至1 MPa时, Hg(l)的 ΔU_m、ΔH_m、ΔS_m、ΔA_m和ΔG_m。

解：Hg的摩尔质量 $M = 200.59\ \mathrm{g\cdot mol^{-1}}$

摩尔体积为: $V_\mathrm{m} = \dfrac{M}{\rho} = 14.82\times10^{-6}\ \mathrm{m^3\cdot mol^{-1}}$

$$\alpha_V = (\partial V/\partial T)_p/V = 1.82\times10^{-4}\,\mathrm{K}^{-1}$$

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

据麦克斯韦关系式：$\left(\dfrac{\partial V}{\partial T}\right)_p = -\left(\dfrac{\partial S}{\partial p}\right)_T = V\alpha_V$

$$\mathrm{d}S_\mathrm{m} = -V_\mathrm{m}\alpha_V\,\mathrm{d}p$$

$$\Delta S_\mathrm{m} = -\int_{p_1}^{p_2} V_\mathrm{m}\alpha_V\,\mathrm{d}p = -V_\mathrm{m}\alpha_V\Delta p = -2.43\times10^{-3}\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$$

例 3.7.1 已知25 ℃时液体汞 Hg(l)的体膨胀系数 $\alpha_V = 1.82\times10^{-4}\ \mathrm{K^{-1}}$，密度 $\rho = 13.534\times10^3\ \mathrm{kg\cdot m^{-3}}$。设外压改变时液体汞的体积不变。求在 25℃ 压力从 100 kPa 增至 1 MPa 时，Hg(l)的 ΔU_m，ΔH_m，ΔS_m，ΔA_m 和 ΔG_m。

$\mathrm{d}T = 0$，$\mathrm{d}V_\mathrm{m} \approx 0$。

$$\Delta U_\mathrm{m} = \int_{S_1}^{S_2} T\mathrm{d}S_\mathrm{m} = T\Delta S_\mathrm{m} = 298.15\ \mathrm{K}\times(-2.43\times10^{-3})\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$$
$$= -0.72\ \mathrm{J\cdot mol^{-1}}$$

$$\Delta A_m = 0$$

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

$$\Delta H_\mathrm{m} = \int_{S_1}^{S_2} T\mathrm{d}S_\mathrm{m} + \int_{p_1}^{p_2} V_\mathrm{m}\mathrm{d}p = T\Delta S_\mathrm{m} + V_\mathrm{m}\Delta p$$
$$= \{298.15\times(-2.43\times10^{-3}) + 14.82\times10^{-6}\times(1-0.1)\times10^6\}\ \mathrm{J\cdot mol^{-1}}$$
$$= 12.62\ \mathrm{J\cdot mol^{-1}}$$

$$\Delta G_\mathrm{m} = \int_{p_1}^{p_2} V_\mathrm{m}\mathrm{d}p = V_\mathrm{m}\Delta p = 14.82\times10^{-6}\mathrm{m^3\cdot mol^{-1}}\times(1-0.1)\times10^6\ \mathrm{Pa}$$
$$= 13.34\ \mathrm{J\cdot mol^{-1}}$$

（2） 热力学函数关系式证明

推导和证明热力学函数关系式，熟悉掌握

★状态函数的定义式：$A = U - TS$，$G = H - TS$，$H = U + pV$

★热力学基本方程式:

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

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

★麦克斯韦关系式

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

★其它关系式

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{nC_{V,\mathrm{m}}}{T} \qquad \left(\frac{\partial S}{\partial T}\right)_p = \frac{nC_{p,\mathrm{m}}}{T} \qquad \left(\frac{\partial z}{\partial x}\right)_y \cdot \left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x = -1$$

★热力学状态方程

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

★热力学状态方程证明 $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p}$ $\boxed{\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p}$

由基本公式 $dU = TdS - pdV$，在定温下除以 dV，得 $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$

据麦克斯韦关系式 $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ 得 $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p}$ 热力学状态方程

对于理想气体，$p = nRT/V$，则 $\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$

所以 $\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{nR}{V} - p = 0$

说明理想气体的热力学能与体积无关，由此从理论上证明了焦耳实验是热力学第一、二定律的必然结果。

同理，由 $dH = TdS + Vdp$ 可以得到 $\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$

根据麦克斯韦关系式 $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ 得 $\boxed{\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p}$ 热力学状态方程

对于理想气体，必然得到 $\left(\frac{\partial H}{\partial p}\right)_T = 0$

例3.7.3　求证： $\mathrm{d}S = \dfrac{nC_{p,\mathrm{m}}}{T}\mathrm{d}T - \left(\dfrac{\partial V}{\partial T}\right)_p \mathrm{d}p$

证明： 设　$S = f(T, p)$

则　$\mathrm{d}S = \left(\dfrac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\dfrac{\partial S}{\partial p}\right)_T \mathrm{d}p$

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

麦克斯韦关系式: $-\left(\dfrac{\partial S}{\partial p}\right)_T = \left(\dfrac{\partial V}{\partial T}\right)_p$

$$\because \left(\frac{\partial S}{\partial T}\right)_p = \frac{nC_{p,\mathrm{m}}}{T}$$

$$\therefore \mathrm{d}S = \frac{nC_{p,\mathrm{m}}}{T}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p$$

例　求证：$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p$

证明：由 $C_{p,\mathrm{m}} = \left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p$ 及 $\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_p = \frac{C_{p,\mathrm{m}}}{T}$ 得 $C_{p,\mathrm{m}} = \left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p = T\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_p$

由 $C_{V,\mathrm{m}} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V$ 及 $\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_V = \frac{C_{V,\mathrm{m}}}{T}$ 得 $C_{V,\mathrm{m}} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V = T\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_V$

于是 $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = T\left\{\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_p - \left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_V\right\}$

$S_\mathrm{m} = f\,(T, V_\mathrm{m})$　　$\mathrm{d}S_\mathrm{m} = \left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \mathrm{d}V_\mathrm{m}$

$$\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_p = \left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_V + \left(\frac{\partial S_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p$$

得 $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = T\left(\frac{\partial S_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p$

利用麦克斯韦关系式 $\left(\frac{\partial S_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$\boxed{C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p}$$