热力学方程组

1. 态函数

$$\begin{cases} U & \text{内能} \\ H \equiv U + pV & \text{焓} \\ F \equiv U - TS & \text{自由能} \\ G \equiv F + pV = U - TS + pV & \text{吉布斯函数} \end{cases}$$

2. 热力学方程

$$\begin{cases} dU = TdS - pdV & \text{—— 热力学基本方程.} \\ dH = TdS + Vdp \\ dF = -SdT - pdV \\ dG = -SdT + Vdp \end{cases}$$

3. Maxwell 关系式

基本关系： $Z_{xy} = Z_{yx}$

记号：将 $\left(\frac{\partial Z}{\partial x}\right)_y$ 记成 $Z_{x,(y)}$

$$\begin{cases} T_{V,(S)} = -p_{S,(V)} \\ T_{p,(S)} = V_{S,(p)} \\ S_{V,(T)} = p_{T,(V)} \\ S_{p,(T)} = -V_{T,(p)} \end{cases}$$

4. 热力学响应函数

$$\begin{cases} C_V = T S_{T,(V)} \\ C_p = T S_{T,(p)} \end{cases}$$

$$\begin{cases} \text{膨胀系数} & \alpha = \frac{1}{V} V_{T,(p)} \\ \text{压强系数} & \beta = \frac{1}{p} p_{T,(V)} \end{cases} \qquad \begin{cases} \text{等温压缩率：} & \kappa_T = -\frac{1}{V} V_{p,(T)} \\ \text{绝热压缩率：} & \kappa_S = -\frac{1}{V} V_{p,(S)} \end{cases}$$

响应函数间关系：

① $S_{T,(p)} = S_{T,(V)} + S_{V,(T)} V_{T,(p)}$

$\Rightarrow C_p = C_V + T p_{T,(V)} V_{T,(p)} = C_V + pVT\alpha\beta$

② $\frac{\kappa_S}{\kappa_T} = \frac{C_V}{C_p}$

5、开放系统的热力学基本方程

定义：巨势 $\Psi = F - \mu N$

$$
\begin{cases}
dU = TdS - pdV + \mu dN \\
dH = Tds + Vdp + \mu dN \\
dF = -SdT - pdV + \mu dN \\
dG = -SdT + Vdp + \mu dN \\
d\Psi = -SdT - pdV - Nd\mu
\end{cases}
$$

补：热力学基本方程及其应用

热一：$đQ = dU - dW = dU + p\,dV$

热二：$đQ = T\,dS$　　(可逆过程)

$\Rightarrow$ TdS 方程 $\begin{cases} T\,dS = dU + p\,dV \\ T\,dS = dH - V\,dp \end{cases}$

1° 内能的偏导数

$U(S,V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = T\,dS - p\,dV$$

2° 焓的偏导数

$H(S,p)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp = T\,dS + V\,dp$$

3° 熵的偏导数

$$\begin{cases} C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \\ C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \end{cases}$$

$$\Rightarrow \begin{cases} \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \\ \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \end{cases}$$

4° 内能与状态方程间的关系.

$$\begin{cases} dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ T\,dS = dU + p\,dV \end{cases}$$

$$\Rightarrow dU = C_V\,dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV$$

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

由Maxwell关系式

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

5° 焓与状态方程间的关系

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

由Maxwell关系式

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

6° Maxwell关系式

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y$$

由1°知 $\left(\frac{\partial}{\partial V} T\right)_S = -\left(\frac{\partial}{\partial S} p\right)_V$

由2°知 $\left(\frac{\partial}{\partial p} T\right)_S = \left(\frac{\partial}{\partial S} V\right)_p$

由2个SdT方程还有

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

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

注：由上述关系可以推出范德瓦尔斯气体的内能与熵.

(摩尔内能)　$U(T,V) = C_V T - \frac{a}{V} + U_0$

(摩尔熵)　$S(T,V) = C_V \ln T + R\ln(V-b) + S_0$