第二章 均匀物质的热力学性质

1. 基本热力学函数
2. 麦氏关系及应用
3. 气体节流和绝热膨胀

§ 2.1 内能、焓、自由能和吉布斯函数的全微分

一、热力学函数

1.基本热力学函数

温度T：宏观定义和微观定义
内能U：宏观定义和微观定义
熵S：宏观定义和微观定义

2.辅助热力学函数

焓：$H=U+pV$
自由能：$F=U-TS$
吉布斯函数:$G=U-TS+pV$

二、热力学函数的全微分

利用热力学基本等式和H.F.G的定义式得到

$$\begin{cases} dU = TdS - pdV \\ dH = TdS + Vdp \\ dF = -SdT - pdV \\ dG = -SdT + Vdp \end{cases}$$

$F = U - TS$

$dF = dU - TdS - SdT$

$\quad = TdS - pdV - TdS - SdT$

$\therefore dF = -SdT - pdV$

$dH = dU + pdV + Vdp$

$\quad = TdS - pdV + pdV + Vdp$

$\therefore dH = TdS + Vdp$

$G = U - TS + pV$

$dG = dU - TdS - SdT + pdV + Vdp$

$\quad = TdS - pdV - TdS - SdT + pdV + Vdp$

$dG = -SdT + Vdp$

记忆方法：

$$(T,S)\left|\begin{cases} TdS \\ -SdT \end{cases}\right. \qquad (p,V)\left|\begin{cases} -pdV \\ Vdp \end{cases}\right.$$

三、麦克斯韦关系推导

1.内能

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

$$U = U(S, V), \quad \mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

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

$$\frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S, \quad \frac{\partial^2 U}{\partial V \partial S} = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

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

2.焓 $H = U + pV$

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

$$H = H(S,\ p),\quad \mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p$$

$$T = \left(\frac{\partial H}{\partial S}\right)_p = T(S,\ p),\quad V = \left(\frac{\partial H}{\partial p}\right)_S = V(S,\ p)$$

$$\frac{\partial^2 H}{\partial S \partial p} = \frac{\partial T}{\partial p},\qquad \frac{\partial^2 H}{\partial p \partial S} = \frac{\partial V}{\partial S}$$

$$\frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}\qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

3. 自由能 $F = U - TS$

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

$$F = F(T,V), \quad \mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_T \mathrm{d}T$$

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

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

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

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

$$H = U + pV = F - T\left(\frac{\partial F}{\partial T}\right)_V - V\left(\frac{\partial F}{\partial V}\right)_T$$

4. 吉布斯函数（自由焓） $G = H - TS = F + pV$

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

$$G = G(T, p), \quad \mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

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

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$

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

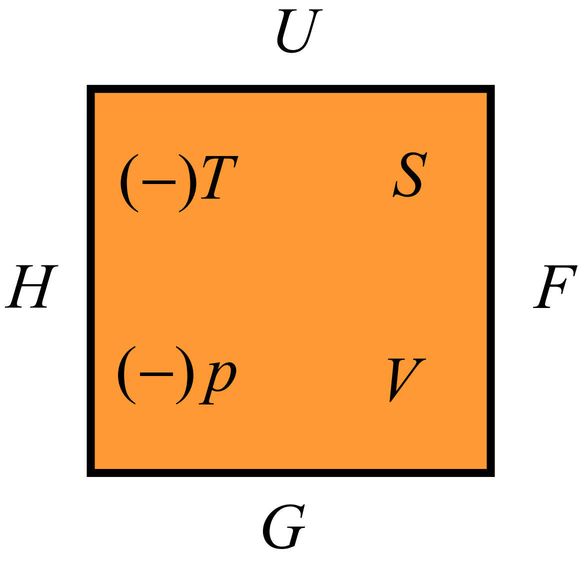
$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_p$$

$$U = H - pV = G - T\left(\frac{\partial G}{\partial T}\right)_p - p\left(\frac{\partial G}{\partial p}\right)_T$$

麦克斯韦关系

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

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



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

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

§2.2 麦氏关系的简单应用

麦克斯韦关系的应用有：

⑴用实验可测量的量（如状态方程，热容量C_p 、 C_v、膨胀系数α、压缩系数κ_r等）表示不能直接测量的量（如U、H、F、G等）（§2.2的内容）

⑵用实验可以测量的量表示某些物理效应及物理量的变化率（§2.3的内容）

⑶求基本热力学函数和特性函数，进而求出所有热力学函数（§2.3、§2.4的内容）

⑷讨论某些物质的热力学性质（§2.6、§2.7的内容）

1. 能态方程与C_V

选择T, V为独立变量，内能和熵均可写成态变量T和V的函数

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

$$S = S(T, V), \quad \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

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

$$\mathrm{d}U = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]\mathrm{d}V$$

$$U = U(T, V), \quad \mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

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

$$\mathrm{d}U = C_V \mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V \qquad \mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V$$

讨论：

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

(1) 对于理想气体， $pV = nRT$

显然有，$\left(\frac{\partial U}{\partial V}\right)_T = 0$ 焦耳定律的结果

(2) 对于范氏气体（1 mol）

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

则有：$\left(\frac{\partial U}{\partial v}\right)_T = T\frac{R}{v-b} - p = \frac{a}{v^2}$

实际气体的内能不仅与温度有关，而且与体积有关。

2. 焓态方程与C_p

以T，p 为独立变量，则有

焓 $$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

$$S = S(T, p), \quad \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

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

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

$$H = H(T, p), \quad \mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$$

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

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

$$\mathrm{d}H = C_p\mathrm{d}T + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p$$

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

* 雅可比行列式

设u，v是自变量（x，y）的函数u（x，y），v（x，y）

雅可比行列式定义：

$$\frac{\partial(u,v)}{\partial(x,y)}=\begin{vmatrix}\left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x\end{vmatrix}=\left(\frac{\partial u}{\partial x}\right)_y\left(\frac{\partial v}{\partial y}\right)_x-\left(\frac{\partial u}{\partial y}\right)_x\left(\frac{\partial v}{\partial x}\right)_y$$

性质：

1. $\left(\frac{\partial u}{\partial x}\right)_y=\left(\frac{\partial(u,y)}{\partial(x,y)}\right)$

2. $\frac{\partial(u,v)}{\partial(x,y)}=-\frac{\partial(v,u)}{\partial(x,y)}=-\frac{\partial(u,v)}{\partial(y,x)}$

3. $\frac{\partial(u,v)}{\partial(x,y)}=\dfrac{\frac{\partial(u,v)}{\partial(r,s)}}{\frac{\partial(x,y)}{\partial(r,s)}}$

4. $\frac{\partial(u,v)}{\partial(x,y)}=\dfrac{1}{\frac{\partial(x,y)}{\partial(u,v)}}$

试求，简单系统的 $Cp - CV =$？

法一：用隐函数的方法

$$C_p - C_V = T\left[\left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V\right]$$

熵可写成 $S(T, p) = S(T, V(T, p))$

$$S = S(T, V), \quad \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

$$S = S(T, p), \quad \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

$$V = V(T, p), \quad \mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p$$

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

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

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

由物态方程决定。

法二：雅可比行列式

$$C_p - C_V = T\left[\left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V\right] = T\left[\left(\frac{\frac{\partial(S,p)}{\partial(T,V)}}{\frac{\partial(T,p)}{\partial(T,V)}}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V\right]$$

$$= T\left[\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T}\begin{vmatrix}\left(\frac{\partial S}{\partial T}\right)_V & \left(\frac{\partial S}{\partial V}\right)_T \\ \left(\frac{\partial p}{\partial T}\right)_V & \left(\frac{\partial p}{\partial V}\right)_T\end{vmatrix} - \left(\frac{\partial S}{\partial T}\right)_V\right]$$

$$= T\left\{\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T}\left[\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\right] - \left(\frac{\partial S}{\partial T}\right)_V\right\}$$

$$= -\frac{T}{\left(\frac{\partial p}{\partial V}\right)_T}\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial p}{\partial T}\right)_V = -\frac{T}{\left(\frac{\partial p}{\partial V}\right)_T}\left(\frac{\partial p}{\partial T}\right)_V^2$$

书上例二的结果

$$C_p - C_V = -\frac{T}{\left(\frac{\partial p}{\partial V}\right)_T}\left(\frac{\partial p}{\partial T}\right)_V^2 = -\frac{T}{\left(\frac{\partial(p,T)}{\partial(V,T)}\right)}\left(\frac{\partial p}{\partial T}\right)_V \frac{\partial(p,V)}{\partial(T,V)}$$

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

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

体胀系数 $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

等温压缩系数 $$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

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

$$C_p - C_V = \frac{VT\alpha^2}{\kappa_T} \geq 0$$

$$\gamma \geq 1$$

以上几式，对于任意简单系统均适用。但C_p-C_V=nR只是理想气体的结论。

等温和绝热压缩系数(书上例一)

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

$$\frac{\kappa_T}{\kappa_S} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S} = \frac{\frac{\partial(V,T)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(p,S)}} = \frac{\frac{\partial(V,T)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(p,S)}} = \frac{\frac{\partial(p,S)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(V,T)}} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V}$$

$$= \frac{C_p}{C_V}$$

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

平衡稳定性要求：以上四量皆为正。

作业：

P73　　2.1题，2.2题，2.3题，2.4题