第二章　均匀物质的热力学性质

§2.1内能、焓、自由能和吉布斯函数的全微分

一、U，H，F，G的全微分

描述热力学系统的态参量有八个

V, T , P, S, U , H, F, G

T，P，V，S非能量性质的参量，常选作独立变量，称为初级变量

U，H，F，G是能量性质的变量。

对于均匀系，无外场，只需要两个独立变量。

取

$$U=U(S,V)$$
$$H=H(S,P)$$
$$F=F(T,V)$$
$$G=G(P,T)$$

由热力学基本方程 $$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \qquad (1)$$

H,F,G定义 H=U+PV

F=U-TS

G=H-TS

对上述式求微分，代入热力学基本方程

例如 $$H = U + pV$$

因为 $$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

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

所以 $$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \qquad (2)$$

（3）　$$\mathrm{d}F = -SdT - p\mathrm{d}V$$

（4）　$$\mathrm{d}G = -SdT + V\mathrm{d}P$$

－－－－此四式称为克劳休斯方程组

U，H，F，G式态函数 ,取全微分

U=U(S,V)　$$dU = \left(\frac{\partial U}{\partial S}\right)_v dS + \left(\frac{\partial U}{\partial V}\right)_s dV$$

H=H(S,P)　$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial P}\right)_s dP$$

F=F(T,V)　$$dF = \left(\frac{\partial F}{\partial T}\right)_v dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

G=G(P,T)　$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

上述四个方程和克劳修斯方程组，比较两方程系数得:

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

$$P=-\left(\frac{\partial U}{\partial V}\right)_s=-\left(\frac{\partial F}{\partial V}\right)_T$$

$$V=\left(\frac{\partial H}{\partial P}\right)_s=\left(\frac{\partial G}{\partial P}\right)_T$$

$$S=-\left(\frac{\partial F}{\partial T}\right)_v=-\left(\frac{\partial G}{\partial T}\right)_P$$

二、麦氏关系式

在数学上， $f = f(x, y)$ 有全微分

$$df = M(x, y)dy + N(x, y)dx$$

是全微分，则必须满足充要条件。

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

热力学函数是状态函数，数学上具有全微分性质，将上述关系式用到四个基本公式中，就得到**Maxwell**关系式：

$$df = M(x,y)dy + N(x,y)dx$$

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

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

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$$

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

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_P$$

(1) $dU = TdS - pdV$

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

(2) $dH = TdS + Vdp$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

(3) $dF = -SdT - pdV$

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

(4) $dG = -SdT + VdP$

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

---称为麦克斯韦关系式

§2.2 麦氏关系的简单应用

例1，证明 $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

证明：

$$dU = \underline{TdS} - PdV = T\left[\underline{\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV}\right] - PdV$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right]dV \qquad \text{--------(1)}$$

因为 $$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{---------(2)}$$

比较系数，得 $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

由麦氏关系 $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

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

① 对理想气体 PV=nRT 得 $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$ ————焦耳定律

② 对范氏气体 $$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

得 $$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V - b} - P = \frac{a}{V^2}$$

例2，证明 $$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

证：选T，P为独立变量

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (1)$$

因为 $$dH = \underline{TdS} + VdP$$

S（T，P） $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

得 $$dH = T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V.\right] dP \qquad (2)$$

比较（1），（2）式 $$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

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

由麦氏关系 $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

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

例3，求Cp-Cv=?

$$C_P = \left(\frac{\text{đ}Q}{dT}\right)_P = \left(\frac{TdS}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_V = \left(\frac{\text{đ}Q}{dT}\right)_v = \left(\frac{TdS}{dT}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_V$$

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

考虑复合函数 $S = S[T, V(T, P)]$

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

所以 $$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

利用麦氏关系 $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

如对理想气体 $C_P - C_V = nR$

§2.5 特性函数

特征函数：如果适当选择独立变量（称为自变量），只要知道一个热力学函数，就可求偏导而求得均匀热力学系统得热力学函数，从而把均匀系统的平衡性质完全确定，这个热力学函数称为特性函数或特征函数。

共八个参量S,V,P,T,U,H,F,G

U(S,V) H(S,P) F(T,V),G（T,P）四个态函数，

只要它们的独立变量按以上规定选择，就可以通过一个态函数把五个参量全部表示出来.

例1，特征函数 F—F（T，V）

由 §2.1得

$$P=-\left(\frac{\partial F}{\partial V}\right)_T \qquad \text{------(1)}$$

$$S=-\left(\frac{\partial F}{\partial T}\right)_v \qquad \text{------(2)}$$

$$U=F+TS=F-T\left(\frac{\partial F}{\partial T}\right)_v \qquad \text{------(3)}$$

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

$$G=H-TS=F-V\left(\frac{\partial F}{\partial V}\right)_T$$

例2，特征函数G＝G（T，P）

$$V=\left(\frac{\partial G}{\partial P}\right)_T \qquad S=-\left(\frac{\partial G}{\partial T}\right)_P$$

$$U=G-PV+TS=G-P\left(\frac{\partial G}{\partial P}\right)_T-T\left(\frac{\partial G}{\partial T}\right)_P$$

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

$$F=U-TS=G-P\left(\frac{\partial G}{\partial P}\right)_T$$

称为吉布斯——亥母霍兹方程

$$U=F-T\left(\frac{\partial F}{\partial T}\right)_v \qquad H=G-T\left(\frac{\partial G}{\partial T}\right)_P$$

§ 2.6 开放系统热力学基本方程

设系统由K个独立组元组成，其特性函数（U，H，F，G）都是P，T，V，S中特定两个变量及各组摩尔数，

$n_1, n_2, \ldots\ldots n_i \ldots\ldots n_k$的函数，即

$U = U(S, V, n_1, n_2, \ldots\ldots n_i \ldots\ldots n_k)$

有 $$dU = \left(\frac{\partial U}{\partial S}\right)_{V,ni} dS + \left(\frac{\partial U}{\partial V}\right)_{s,ni} dV + \sum_{i=1}^{k}\left(\frac{\partial U}{\partial ni}\right)_{V,s,nj} dni \qquad (j \neq i)$$

又 $$dU = TdS - PdV + \sum \mu_i dni$$

对组元不变的系统 $$\left(\frac{\partial U}{\partial S}\right)_{V,ni} = T$$

$$\left(\frac{\partial U}{\partial V}\right)_{s,ni} = -P$$

令 $$\mu_i = \left(\frac{\partial U}{\partial ni}\right)_{s,v,nj}$$ ———第I种组元的化学势

于是 $$dU = TdS - PdV + \sum_{i=1} \mu_i dni$$ ———开放系统热力学方程

相应有 $$dH = TdS + VdP + \sum_{i=1}^{k} \mu_i dni$$

$$dF = -SdT - PdV + \sum_{i=1}^{k} \mu_i dni$$

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dni$$

应有

$$\mu_i = \left(\frac{\partial U}{\partial ni}\right)_{s,v,nj} = \left(\frac{\partial H}{\partial ni}\right)_{s,P,nj} = \left(\frac{\partial F}{\partial ni}\right)_{T,v,nj} = \left(\frac{\partial G}{\partial ni}\right)_{T,P,nj}$$

μi 的意义

$$dU = TdS - PdV + \sum_{i=1}^{k} \mu_i dni$$

前两项是在T，P这两项强度量下引起能量的传递，

μi **是引起物质迁移而使能量发生改变的强度量，叫化学势。表征某组元的物质由系统向外界逃逸或迁移的能力。**