第二章
均匀物质的热力学性质

热力学常用的数学结果

1、偏导数和全微分

若z是独立变数x，y的函数 $z = z(x, y)$

则z的全微分

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

2、隐函数

若有函数关系 $z = z(x, y)$

则有隐函数 $F(x, y, z) = 0$

$$dF = \frac{\partial F}{\partial x}dx + \frac{\partial F}{\partial y}dy + \frac{\partial F}{\partial z}dz = 0$$

$$dy = 0, \left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\frac{\partial F}{\partial x}\right)_{y,z}}{\left(\frac{\partial F}{\partial z}\right)_{y,x}}, \left(\frac{\partial x}{\partial z}\right)_y = -\frac{\left(\frac{\partial F}{\partial z}\right)_{y,x}}{\left(\frac{\partial F}{\partial x}\right)_{y,z}},$$

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_y = 1 \Big/ \left(\frac{\partial x}{\partial z}\right)_y}$$

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1}$$

3、复合函数

•若有函数关系 $z = z(x, y)$

且x、y又都是t的函数，则z实际上也是t的函数

$$\frac{dz}{dt} = \frac{\partial z}{\partial x}\frac{dx}{dt} + \frac{\partial z}{\partial y}\frac{dy}{dt}$$

•若有函数关系 $z = z(x, y)$

且 $x = x(u, v)$ $y = y(u, v)$ 则 $z = z(u, v)$

$$\frac{\partial z}{\partial u} = \frac{\partial z}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial z}{\partial y}\frac{\partial y}{\partial u}$$

$$\frac{\partial z}{\partial v} = \frac{\partial z}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial z}{\partial y}\frac{\partial y}{\partial v}$$

• 若 $u = x$

即 $z = z(x, y) \qquad y = y(x, v)$

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

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

4、雅可比行列式

- 若 $u = u(x, y) \quad v = v(x, y)$

雅可比行列式定义为

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \dfrac{\partial u}{\partial x}, & \dfrac{\partial u}{\partial y} \\ \dfrac{\partial v}{\partial x}, & \dfrac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}$$

•雅可比行列式的性质：

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

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

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(x,s)}\frac{\partial(x,s)}{\partial(x,y)}$$

$$\frac{\partial(u,v)}{\partial(x,y)} = 1\Big/\frac{\partial(x,y)}{\partial(u,v)}$$

4、完整微分条件和积分因子

•若有函数关系 $z = z(x, y)$

则z的全微分

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Xdx + Ydy$$

其中X、Y也是x、y的函数，再次求导

$$\frac{\partial X}{\partial y} = \frac{\partial}{\partial y}\frac{\partial z}{\partial x} = \frac{\partial^2 z}{\partial y \partial x}$$

$$\frac{\partial Y}{\partial x} = \frac{\partial}{\partial x}\frac{\partial z}{\partial y} = \frac{\partial^2 z}{\partial x \partial y}$$

$$\Rightarrow \quad \frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x}$$

•反之，设有微分式

$$dz = X(x,y)dx + Y(x,y)dy$$

函数z的全微分

若满足条件

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x}$$

完整微分条件

则上式为函数z（x，y）的全微分。

完整微分的性质：

$$\int_A^B dz = \int_A^B X(x,y)dx + Y(x,y)dy = z(B) - z(A)$$

$$\oint dz = \oint Xdx + Ydy = 0$$

§ 2.1 U、H、F、G的全微分

1. 内能

状态参量：（P, V, T）

（P, V），（P, T），（V, T）（只有两个自由变量）

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

$$U = U(S, V)$$

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

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

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

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

问题的提出

$$H = U + pV$$

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

$$\Downarrow$$

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

2. 焓 $H = U + pV$ $\quad \mathbf{dH = TdS - pdV + pdV + Vdp}$

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

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

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

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

问题的提出

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

$$\Downarrow$$

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

3. 自由能

$F = U - TS \quad dF = TdS - pdV - TdS - SdT$

$$\boxed{dF = -SdT - pdV} \qquad F = F(T, V)$$

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

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

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

问题的提出

$$G = H - TS = F + pV$$

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

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

4. 吉布斯函数（自由焓） $G = U - TS + pV$

$$dG = TdS - pdV - TdS - SdT + pdV + Vdp \qquad \boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p}$$

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

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

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p} \qquad \boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p}$$

$$dU = TdS - pdV$$

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

$$dH = TdS + Vdp$$

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

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

$$dF = -SdT - pdV$$

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

$$dG = -SdT + Vdp$$

§2.2　麦氏关系及应用

1. 麦克斯韦关系

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

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

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

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

麦克斯韦关系将不能直接在实验上测量的量用可以在实验上直接测量的量表示出来

不能直接测量的量　　**S, U, H, F, G**

可以直接测量的量　　物态方程，热容量，　α 和 κ_T

例1，以T, V为状态参量，求U的全微分

$$dU(T,V)=\left(\frac{\partial U}{\partial T}\right)_V dT+\left(\frac{\partial U}{\partial V}\right)_T dV$$

由热力学基本方程 $dU = TdS - pdV$

并且 $$dS(T,V)=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV$$

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

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

比较得
$$\begin{cases}\left(\dfrac{\partial U}{\partial T}\right)_V = C_V = T\left(\dfrac{\partial S}{\partial T}\right)_V \\ \left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial S}{\partial V}\right)_T - p = T\left(\dfrac{\partial p}{\partial T}\right)_V - p\end{cases}$$

上式中$(\partial p/\partial T)_V$可以通过状态方程来求得

例如

对于理想气体 $$pV_m = RT$$

$$\left(\frac{\partial U_m}{\partial V_m}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_{V_m} - p = 0$$

与焦耳定律的结果一致。

对于范氏气体 $$\left(p + \frac{a}{V_m^{\ 2}}\right)(V_m - b) = RT$$

$$\left(\frac{\partial U_m}{\partial V_m}\right)_T = \frac{RT}{V_m - b} - p = \frac{a}{V_m^{\ 2}}$$

温度不变时范氏气体内能随体积的变化率。

二、以T, p为自变量时焓的全微分：

$$dH(T, p) = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

由 $$dH = TdS + Vdp$$

并且 $$dS(T, p) = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

得 $$dH = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp$$

比较得
$$\begin{cases} \left(\frac{\partial H}{\partial T}\right)_p = C_p = T\left(\frac{\partial S}{\partial T}\right)_p \\ \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p \end{cases}$$

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

三、利用麦氏关系计算任意简单系统C_p与C_V之差：

由前结果 $$C_p - C_V = T\left(\frac{\partial S}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_V$$

由函数关系 $$S(T,p) = S\left(T, V(T,p)\right)$$

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

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

此式适用于任意的简单系统。

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

例如

对于理想气体 pV = nRT $C_p - C_V = T(\frac{\partial p}{\partial T})_V(\frac{\partial V}{\partial T})_p = nR$

对于任意简单系统，由于

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_p,\ \beta = \frac{1}{p}(\frac{\partial p}{\partial T})_V,\ \kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial p})_T,\ \text{且}\ \alpha = \kappa_T \beta p$$

所以 $C_p - C_V = T(\frac{\partial p}{\partial T})_V(\frac{\partial V}{\partial T})_p = Tp\beta V\alpha = \frac{VT\alpha^2}{\kappa_T}$

可见 $C_p - C_V \geq 0$ 。实验上难以测量固体和液体的定容热容量，则可以根据上式利用其它可测量计算出来。

四、利用雅各比行列式进行导数变换：

定义

$$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{vmatrix} \dfrac{\partial u}{\partial x} & \dfrac{\partial u}{\partial y} \\ \dfrac{\partial v}{\partial x} & \dfrac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}$$

性质

$$\boxed{\begin{aligned} &\left(\frac{\partial u}{\partial x}\right)_y = \frac{\partial(u,y)}{\partial(x,y)} \\ &\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} \\ &\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(x,s)}\frac{\partial(x,s)}{\partial(x,y)} \\ &\frac{\partial(u,v)}{\partial(x,y)} = 1\Big/\frac{\partial(x,y)}{\partial(u,v)} \end{aligned}}$$

附录P357-358

【例一】 求证绝热压缩系数(κ_s)与等温压缩系数(κ_T)之比等于定容热容量与定压热容量之比(C_V/C_p)。

证明：由定义

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

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

$$\frac{\partial(\boldsymbol{V},\boldsymbol{S})}{\partial(\boldsymbol{p},\boldsymbol{S})}\frac{\partial(\boldsymbol{p},\boldsymbol{T})}{\partial(\boldsymbol{V},\boldsymbol{T})} = \left[\frac{\partial(\boldsymbol{V},\boldsymbol{S})}{\partial(\boldsymbol{V},\boldsymbol{T})}\frac{\partial(\boldsymbol{V},\boldsymbol{T})}{\partial(\boldsymbol{p},\boldsymbol{S})}\right]\frac{\partial(\boldsymbol{p},\boldsymbol{T})}{\partial(\boldsymbol{V},\boldsymbol{T})} = \frac{\partial(\boldsymbol{V},\boldsymbol{S})}{\partial(\boldsymbol{V},\boldsymbol{T})}\frac{\partial(\boldsymbol{p},\boldsymbol{T})}{\partial(\boldsymbol{p},\boldsymbol{S})}$$

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_V = C_V = T\left(\frac{\partial S}{\partial T}\right)_V} \qquad \boxed{\left(\frac{\partial H}{\partial T}\right)_p = C_p = T\left(\frac{\partial S}{\partial T}\right)_p}$$

【例二】求证

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

证明：

$$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}$$

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

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

热力学中一些微分的简化：

目标:将所有热力学函数转化为实验可测变量的表达式，$T, p, V, \alpha, \beta, \kappa_T, C_V, C_p.$

S, U, H, F, G的全微分表达式

	(T,V)	(T,p)	(p,V)
Equation of state	dp(T,V)	dV(T,p)	dT(p,V)
dS	dS(T,V)	dS(T,p)	dS(p,V)
dU	dU(T,V)	dU(T,p)	dU(p,V)
dH	dH(T,V)	dH(T,p)	dH(p,V)
dF	dF(T,V)	dF(T,p)	dF(p,V)
dG	dG(T,V)	dG(T,p)	dG(p,V)

TdS 方程

$$TdS(T,V) = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV,$$

$$TdS(T,p) = T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dV = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp,$$

$$TdS(p,V) = T\left(\frac{\partial S}{\partial p}\right)_V dp + T\left(\frac{\partial S}{\partial V}\right)_p dV = C_V\left(\frac{\partial T}{\partial p}\right)_V dp + C_p\left(\frac{\partial T}{\partial V}\right)_p dV,$$

常用热力学函数的全微分

	(T,V) 为独立变量	(T,p) 为独立变量	(p,V) 为独立变量
dU	$dU=TdS-pdV$ $=C_VdT+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV$	$dU=TdS-pdV$ $=\left[C_p-p\left(\frac{\partial V}{\partial T}\right)_p\right]dT-\left[T\left(\frac{\partial V}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial p}\right)_T\right]dp$	$dU=TdS-pdV$ $=C_V\left(\frac{\partial T}{\partial p}\right)_V dp+\left[C_p\left(\frac{\partial T}{\partial V}\right)_p-p\right]dV$
dH	$dH=TdS+Vdp$ $=\left[C_V+V\left(\frac{\partial p}{\partial T}\right)_V\right]dT+\left[T\left(\frac{\partial p}{\partial T}\right)_V+V\left(\frac{\partial p}{\partial V}\right)_T\right]dV$	$dH=TdS+Vdp$ $=C_pdT+\left[-T\left(\frac{\partial V}{\partial T}\right)_p+V\right]dp$	$dH=TdS+Vdp$ $=\left[C_V\left(\frac{\partial T}{\partial p}\right)_V+V\right]dp+C_p\left(\frac{\partial T}{\partial V}\right)_p dV$
dF	$dF=-SdT-pdV$	$dF=-SdT-pdV$ $=\left[-S-p\left(\frac{\partial V}{\partial T}\right)_p\right]dT-p\left(\frac{\partial V}{\partial p}\right)_T dp$	$dF=-SdT-pdV$ $=-S\left(\frac{\partial T}{\partial p}\right)_V dp-\left[S\left(\frac{\partial T}{\partial V}\right)_p+p\right]dV$
dG	$dG=-SdT+Vdp$ $=\left[-S+V\left(\frac{\partial p}{\partial T}\right)_V\right]dT+V\left(\frac{\partial p}{\partial V}\right)_T dV$	$dG=-SdT+Vdp$	$dG=-SdT+Vdp$ $=\left[-S\left(\frac{\partial T}{\partial p}\right)_V+V\right]dp-S\left(\frac{\partial T}{\partial V}\right)_p dV$
dS	$dS=\frac{C_V}{T}dT+\left(\frac{\partial p}{\partial T}\right)_V dV$	$dS=\frac{C_p}{T}dT-\left(\frac{\partial V}{\partial T}\right)_p dp$	$dS=\frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V dp+\frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p dV$

Maxwell 关系: $\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V$, $\left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_p$, $\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V$, $\left(\frac{\partial S}{\partial p}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_p$, 后两个 Maxwell 关系在化简 (T,V), (T,p), (p,V) 系统时候常用.

其中的函数定义: $C_V=T\left(\frac{\partial S}{\partial T}\right)_V$, $C_p=T\left(\frac{\partial S}{\partial T}\right)_p$, $\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, $\kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$, ($\beta=\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$, $\alpha=\kappa_T\beta p$, $C_p-C_V=-T\left(\frac{\partial p}{\partial T}\right)_V^2\Big/\left(\frac{\partial p}{\partial V}\right)_T$).

物态方程相关偏导数: $\left(\frac{\partial p}{\partial T}\right)_V=\frac{\alpha}{\kappa_T}$, $\left(\frac{\partial T}{\partial V}\right)_p=\frac{1}{V\alpha}$, $\left(\frac{\partial V}{\partial p}\right)_T=-V\kappa_T$; $\left(\frac{\partial V}{\partial T}\right)_p=V\alpha$, $\left(\frac{\partial T}{\partial p}\right)_V=\frac{\kappa_T}{\alpha}$, $\left(\frac{\partial p}{\partial V}\right)_T=-\frac{1}{V\kappa_T}$.

(1) S, U, H, F, G在分数的分子或分母上，我们可以先推导出全微分，然后写出导数

$$dU(T,V) = C_V dT + \left(T\left(\frac{\partial p}{\partial T}\right)_V - p \right) dV,$$

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

(2) S, U, H, F,在下标处，可以首先使用循环关系或雅各比关系，并将问题改为情形(1).

$$dH = C_p dT + \left(-T\left(\frac{\partial V}{\partial T}\right)_p + V \right) dp,$$

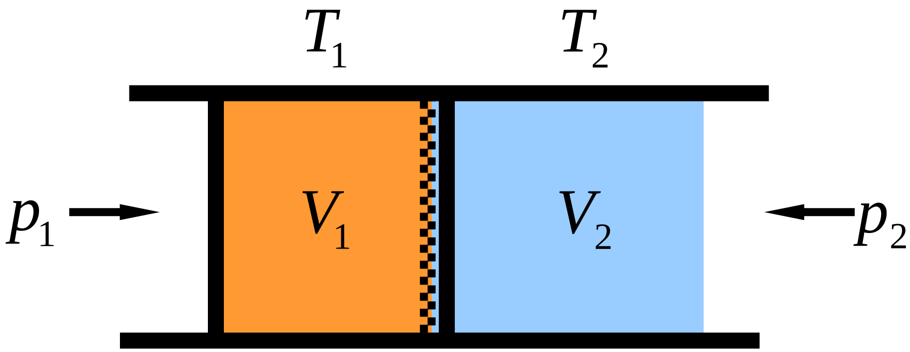
$$\frac{\partial(T,H)}{\partial(p,H)} \frac{\partial(p,T)}{\partial(H,T)} \frac{\partial(H,p)}{\partial(T,p)} = -1,$$

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

§ 2.3 气体节流和绝热膨胀

1. 节流

气体节流后温度改变　　焦—汤效应



外界对系统做功　p_1V_1

系统对外界做功　p_2V_2

$$U_2 - U_1 = p_1V_1 - p_2V_2$$

$$\mathbf{U_2 + p_2V_2 = U_1 + p_1V_1}$$

$$H_2 = H_1$$

气体节流后焓不变。

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

称为焦汤系数。

取***T*, *p***为状态参量，$H = H(T, p)$ 有 $\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p = -1$

$$\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p = -1$$

所以

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{V - T\left(\frac{\partial V}{\partial T}\right)_p}{C_p} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

有：$\left(\frac{\partial H}{\partial T}\right)_p = C_p$ $\qquad$ $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$ （2.2.10）

$$\mu = \frac{V}{C_p}\left[\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p - 1\right] = \frac{V}{C_p}(T\alpha - 1)$$

对于理想气体，$\alpha = \frac{1}{T}$，所以 $\mu = 0$，即理气在节流过程前后温度不变。

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial T}\right)_p = \frac{1}{V}\frac{nR}{p} = \frac{1}{T},$$

对于实际气体，若 $\alpha T > 1$，则 $\mu > 0$，即气体经节流过程后降温；若 $\alpha T < 1$，则 $\mu < 0$，即气体经节流过程后升温。

节流过程压强降低

二、绝热膨胀（准静态）

由于绝热过程 $dS = \frac{\cancel{d}Q_R}{T} = 0$ 分析 $(\frac{\partial T}{\partial p})_S$

因为 $(\frac{\partial T}{\partial p})_S (\frac{\partial p}{\partial S})_T (\frac{\partial S}{\partial T})_p = -1$

所以 $$(\frac{\partial T}{\partial p})_S = -\frac{(\frac{\partial S}{\partial p})_T}{(\frac{\partial S}{\partial T})_p} = -\frac{-(\frac{\partial V}{\partial T})_p}{C_p / T} = \frac{TV\alpha}{C_p} \geq 0$$

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

$$\boxed{C_p = T(\frac{\partial S}{\partial T})_p}$$

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

即气体膨胀，压强降低，气体温度必然下降。

§ 2.4 基本热力学函数的确定

最基本的热力学函数是物态方程、内能和熵，其它热力学函数可由此导出。

$$f(p,V,T)=0$$

$$dU=TdS-pdV$$

$$dS=\frac{đQ_R}{T}$$

一、若选T, V为状态参量，已知物态方程为 $p = p(T,V)$

$$dp(T,V) = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV, \quad \Rightarrow \quad p = \int_{(T_0,V_0)}^{(T,V)} dp(T,V) = \ldots,$$

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

(2.2.7)

积分得 $$U = \int \left\{ C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV \right\} + U_0$$

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

积分得 $$S = \int \left\{ \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV \right\} + S_0$$

如果测得物质的C_V和物态方程，可求得其内能和熵。

其他函数 $$H = U + pV, \quad F = U - TS, \quad G = U - TS + pV,$$

二、若选T, p为状态参量，已知物态方程为 $V=V(T,p)$

$$dV(T,p)=\left(\frac{\partial V}{\partial T}\right)_p dT+\left(\frac{\partial V}{\partial p}\right)_T dp, \quad \Rightarrow \quad V=\int_{(T_0,p_0)}^{(T,p)} dV(T,p)=\ldots,$$

由于 $$dH(T,p)=(\frac{\partial H}{\partial T})_p dT+(\frac{\partial H}{\partial p})_T dp=C_p dT+[V-T(\frac{\partial V}{\partial T})_p]dp \quad (2.2.10)$$

积分得 $$H=\int\{C_p dT+[V-T(\frac{\partial V}{\partial T})_p]dp\}+H_0 \qquad U=H-pV$$

而由 $$dS(T,p)=(\frac{\partial S}{\partial T})_p dT+(\frac{\partial S}{\partial p})_T dp=\frac{C_p}{T}dT-(\frac{\partial V}{\partial T})_p dp$$

积分得 $$S=\int\{\frac{C_p}{T}dT-(\frac{\partial V}{\partial T})_p dp\}+S_0$$

如果测得物质的C_p和物态方程，可求得其内能和熵。

其他函数 $H=U+pV, \quad F=U-TS, \quad G=U-TS+pV,$

求热力学函数的一般方法：

(1)求所需函数的全微分方程的导数

	(T,V)	(T,p)	(p,V)
Equation of state	dp(T,V)	dV(T,p)	dT(p,V)
dS	dS(T,V)	dS(T,p)	dS(p,V)
dU	dU(T,V)	dU(T,p)	dU(p,V)
dH	dH(T,V)	dH(T,p)	dH(p,V)
dF	dF(T,V)	dF(T,p)	dF(p,V)
dG	dG(T,V)	dG(T,p)	dG(p,V)

(2)对全微分方程进行积分，或采用收凑全微分的方法.

【例一】 以T, p为状态参量，求理想气体的焓、熵和吉布斯函数。

解：1mol理想气体 $pV_m = RT$

所以 $$H_m = \int \{C_p dT + [V_m - T(\frac{\partial V_m}{\partial T})_p]dp\} + H_{m0}$$

$$= \int C_{p,m} dT + H_{m0}$$

$$= C_{p,m} T + H_{m0}$$（若$C_{p,m}$可看作常数）

$$S_m = \int \{\frac{C_{p,m}}{T} dT - (\frac{\partial V_m}{\partial T})_p dp\} + S_{m0}$$

$$= \int \frac{C_{p,m}}{T} dT - R\ln p + S_{m0}$$

$$= C_{p,m} \ln T - R\ln p + S_{m0}$$（若$C_{p,m}$可看作常数）

由于

$$G_m = H_m - TS_m$$

所以

$$G_m = \int C_{p,m} dT - T\int \frac{C_{p,m}}{T} dT + RT\ln p + H_{m0} - TS_{m0}$$

$$= C_{p,m}T - C_{p,m}T\ln T + RT\ln p + H_{m0} - TS_{m0}$$（若$C_{p,m}$可看作常数）

利用 $\int xdy = xy - \int ydx$ 令$x = \frac{1}{T}$, $y = \int C_{p,m} dT$

$$\int \frac{1}{T} C_{p,m} \mathrm{d}T = \frac{1}{T}\int C_{p,m}\mathrm{d}T - \int\left(\int C_{p,m}\mathrm{d}T\right)\mathrm{d}\frac{1}{T},$$

$$\Rightarrow T\int \frac{C_{p,m}}{T}\mathrm{d}T = \int C_{p,m}\mathrm{d}T + T\int \frac{1}{T^2}\mathrm{d}T\int C_{p,m}\mathrm{d}T.$$

$$G_m = -T\int \frac{dT}{T^2}\int C_{p,m}dT + RT\ln p + H_{m0} - TS_{m0}$$

通常写成 $G_m = RT(\varphi + \ln p)$ 其中 φ 为温度的函数。

$$\varphi = \frac{H_{m0}}{RT} - \int \frac{dT}{RT^2}\int C_{p,m}dT - \frac{S_{m0}}{R}$$

其他求解方法: $c_p = const.,$

$$dS(T,p)=\frac{C_p}{T}dT-\left(\frac{\partial V}{\partial T}\right)_p dp=\frac{C_p}{T}dT-\frac{nR}{p}dp,$$

$$S=\int_{(T_0,p_0)}^{(T,p)}dS=\int_{(T_0,p_0)}^{(T,p)}\frac{C_p}{T}dT-\frac{nR}{p}dp=\int_{(T_0,p_0)}^{(T,p_0)}\frac{C_p}{T}dT-\int_{(T,p_0)}^{(T,p)}\frac{nR}{p}dp$$

$$=C_p\ln T-nR\ln p-C_p\ln T_0+nR\ln p_0=C_p\ln T-nR\ln p+S_0,$$

$$dG(T,p)=-SdT+Vdp=-(C_p\ln T-nR\ln p+S_0)dT+\frac{nRT}{p}dp,$$

$$G=\int_{(T_0,p_0)}^{(T,p)}dG(T,p)=\int_{(T_0,p_0)}^{(T,p)}\left[-(C_p\ln T-nR\ln p+S_0)dT+\frac{nRT}{p}dp\right]$$

$$=\left(-\int_{(T_0,p_0)}^{(T,p_0)}(C_p\ln T-nR\ln p+S_0)dT\right)+\left(\int_{(T,p_0)}^{(T,p)}\frac{nRT}{p}dp\right)$$

$$=-\int_{(T_0,p_0)}^{(T,p_0)}C_p\ln TdT+(nRT\ln p-S_0T)\Big|_{(T_0,p_0)}^{(T,p_0)}+nRT\ln p\Big|_{(T,p_0)}^{(T,p)}$$

$$=-\int_{(T_0,p_0)}^{(T,p_0)}C_p\ln TdT+(\boxed{nRT\ln p_0}-S_0T)-(nRT_0\ln p_0-S_0T_0)+nRT\ln p\boxed{-nRT\ln p_0}$$

$$=-\int_{(T_0,p_0)}^{(T,p_0)}C_p\ln TdT+nRT\ln p-S_0T-(nRT_0\ln p_0-S_0T_0)$$

$$=C_pT-C_pT\ln T+nRT\ln p-S_0T+\boxed{\left[-C_pT_0-C_pT_0\ln T_0-(nRT_0\ln p_0-S_0T_0)\right]}$$

$$=C_pT-C_pT\ln T+nRT\ln p-S_0T+G_0$$

例2: 求范德瓦尔斯气体的内能和熵.

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

$$\left(\frac{\partial p}{\partial T}\right)_V=\frac{R}{\upsilon-b}\rightarrow T\left(\frac{\partial p}{\partial T}\right)_V-p=\frac{a}{\upsilon^2}$$

$$u=\int\left\{c_V dT+\left[T\left(\frac{\partial T}{\partial p}\right)_V-p\right]dV\right\}+u_0=\int c_V dT-\frac{a}{\upsilon}+u_0$$

$$s=\int\left[\frac{c_V}{T}dT+\left(\frac{\partial p}{\partial T}\right)_V dV\right]+s_0=\int\frac{c_V}{T}dT+R\ln(\upsilon-b)+s_0$$

其他热力学函数:

$H=U+pV,$ $F=U-TS,$ $G=U-TS+pV,$

例3 简单固体的物态方程为$\upsilon(T,p)=\upsilon(T_0,0)[1+\alpha(T-T_0)-\kappa_T p]$. 是求其内能和熵.

$$p=\frac{\alpha T}{\kappa_T}-\frac{\upsilon-\upsilon_1}{\kappa_T\upsilon_0},\qquad \upsilon_1=\upsilon_0-\alpha\upsilon_0 T_0$$

$$\left(\frac{\partial p}{\partial T}\right)_V=\frac{\alpha}{\kappa_T},\quad T\left(\frac{\partial p}{\partial T}\right)_V-p=\frac{\upsilon-\upsilon_1}{\kappa_T\upsilon_0}$$

$$u=\int\left\{c_V dT+\left[T\left(\frac{\partial T}{\partial p}\right)_V-p\right]dV\right\}+u_0=\int c_V dT-\frac{1}{2}\frac{(\upsilon-\upsilon_1)^2}{\kappa_T\upsilon_0}+u_0,$$

$$s=\int\left[\frac{c_V}{T}dT+\left(\frac{\partial p}{\partial T}\right)_V dV\right]+s_0=\int\frac{c_V}{T}dT+\frac{\alpha}{\kappa_T}\upsilon+s_0$$

其他热力学函数:

$$H=U+pV,\qquad F=U-TS,\qquad G=U-TS+pV,$$

2.5 特性函数

马休在1869年证明，如果适当选取独立变量，只要知道一个热力学函数，就可通过求偏导数而求得均匀系统的全部热力学函数。从而确定均匀系统的平衡性质，这一热力学函数称为特性函数。

U(S, V), H(S, p), F(T, V), G(T, p)

$U(S,V)$ $\quad dU = TdS - pdV,$

$H(S,p)$ $\quad dH = TdS + Vdp,$

$F(T,V)$ $\quad dF = -SdT - pdV,$

$G(T,p)$ $\quad dG = -SdT + Vdp,$

自由能

由于 $$dF = -SdT - pdV = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

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

若已知***F*(*T*, *V*)**，则可得出***S*(*T*, *V*)**，***p*(*T*, *V*)**。

由 $$F = U - TS$$

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$$ 由此可求***U*(*T*, *V*)**

吉布斯一亥姆霍兹方程。

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

吉布斯函数

由于 $$dG = -SdT + Vdp = (\frac{\partial G}{\partial T})_p dT + (\frac{\partial G}{\partial p})_T dp$$

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

若已知**$G(T, p)$**，则可得出**$S(T, p)$**，**$V(T, p)$**。

由 $$U = G + TS - pV = G - T\frac{\partial G}{\partial T} - p\frac{\partial G}{\partial p}$$ 可求**$U(T, p)$**

由 $$H = U + pV = G + TS = G - T\frac{\partial G}{\partial T}$$ 可求**$H(T, p)$**

吉布斯—亥姆霍兹方程。

例：已知 $U=U(S,V)$ 求系统的其它热力学函数

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

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

$$H=U+pV=U-V\left(\frac{\partial U}{\partial V}\right)_S$$

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

$$G=U-TS+pV=U-S\left(\frac{\partial U}{\partial S}\right)_V-V\left(\frac{\partial U}{\partial V}\right)_S$$

【例】 求表面系统的热力学函数。

解：表面系统的物态方程 $f(\sigma, A, T) = 0$

其中 $\sigma = \sigma(T)$

当面积有**dA**的改变，外界作功 $đW = \sigma dA$

所以 $$dF = -SdT + \sigma dA$$

$$S = -\frac{\partial F}{\partial T}, \ \sigma = \frac{\partial F}{\partial A}, \text{得出} F = \sigma A$$

$$S = -A\frac{d\sigma}{dT}, \ U = F + TS = A(\sigma - T\frac{d\sigma}{dT})$$

只要测得 $\sigma(T)$ 即可求得表面系统的热力学函数。

2.6 热辐射的热力学理论

一、平衡热辐射

平衡辐射（空窖辐射，黑体辐射）的特点：

1、吸收和辐射达到平衡；

2、空窖辐射的内能密度和内能密度按频率的分布只取决于温度，与空窖的其它性质无关。

二、平衡辐射的热力学函数

内能 $$U(T,V)=u(T)V$$ 平衡辐射的内能密度只是温度的函数。

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

由 $$p=\frac{1}{3}u \quad \Longrightarrow \quad u(T)=\frac{T}{3}\frac{du}{dT}-\frac{u}{3}$$

由 $p=\frac{1}{3}u$ $\Longrightarrow$ $u(T)=\frac{T}{3}\frac{du}{dT}-\frac{u}{3}$

即 $\frac{du}{u}=4\frac{dT}{T}$ $\Longrightarrow$ $\boxed{u=aT^4}$

$$U(T,V)=u(T)V=aT^4V$$

熵 $$dS=\frac{dU+pdV}{T}=\frac{1}{T}d(aT^4V)+\frac{1}{3}aT^3dV$$

$$=4aT^2VdT+\frac{4}{3}aT^3dV\quad=\frac{4}{3}ad(T^3V)$$

$$S=\frac{4}{3}aT^3V$$

对于非守恒粒子系统，吉布斯函数始终为零

吉布斯函数：

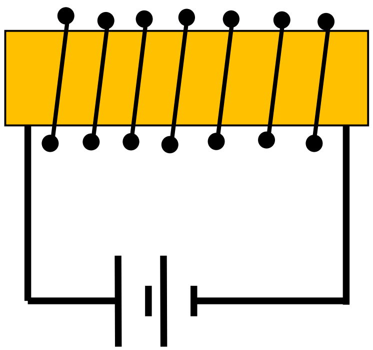
$$G=U-TS+pV=VaT^4-\frac{4}{3}aT^4V+\frac{1}{3}aT^4V=0$$

2.7　磁介质的热力学

磁介质

电动势： V　磁感应强度: B　电流: I

磁场强度: H　磁化强度: M　面积: A



$$đW = VI\mathrm{d}t$$

法拉第定律　$V = N\frac{\mathrm{d}(AB)}{dt}$

安培定理　$\oint Hdl = NI;$ $\longrightarrow$ $Hl = NI$

$$đW = \left(NA\frac{\mathrm{d}B}{dt}\right)\left(\frac{l}{N}H\right)dt = AlHdB = VHdB$$

注意：$B = \mu H = \mu_0(H + M)$

$$đW = VH\mathrm{d}[\mu_0(H + M)] = Vd\left(\frac{\mu_0 H^2}{2}\right) + \mu_0 VHdM$$

2.7 磁介质的热力学

磁致冷却

当磁场强度和磁化强度发生改变时，外界对磁介质所作的功为

$$đW = VH\mathrm{d}[\mu_0(H+M)] = Vd\left(\frac{\mu_0 H^2}{2}\right) + \mu_0 VHdM$$

激发磁场的功　　使介质磁化的功

当热力学系统只包括介质而不包括磁场时，

$$đW = \mu_0 VHdM = \mu_0 Hdm$$

$m = VM$ 是介质的总磁矩。

如果忽略磁介质的体积变化，磁介质的热力学基本方程

$$dU = TdS + \mu_0 Hdm$$

其中作了代换 $p \to -\mu_0 H$，$V \to m$

同样，由 $G = U - TS + pV \Rightarrow G = U - TS - \mu_0 Hm$

由 $dG = -SdT + Vdp \Rightarrow dG = -SdT - \mu_0 mdH$

麦氏关系 $(\frac{\partial S}{\partial p})_T = -(\frac{\partial V}{\partial T})_p \Rightarrow (\frac{\partial S}{\partial H})_T = \mu_0 (\frac{\partial m}{\partial T})_H$

也可由完整微分条件得出。

因为有函数关系 $S = S(T, H)$

有 $$\left(\frac{\partial T}{\partial H}\right)_S \left(\frac{\partial H}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_H = -1$$

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_H$$

$$\Rightarrow \quad \left(\frac{\partial T}{\partial H}\right)_S = -\frac{\left(\frac{\partial S}{\partial H}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_H}$$

引入磁介质的热容量 $C_H = T\left(\frac{\partial S}{\partial T}\right)_H$

$$\Rightarrow \quad \left(\frac{\partial T}{\partial H}\right)_S = -\frac{\mu_0 T}{C_H}\left(\frac{\partial m}{\partial T}\right)_H$$

由居里定律 $\boxed{\mu = \frac{C}{T} H}$ $m = \frac{CV}{T} H$

则 $$(\frac{\partial m}{\partial T})_H = -\frac{CV}{T^2} H$$

所以 $$(\frac{\partial T}{\partial H})_S = \frac{CV}{C_H T} \mu_0 H > 0$$

这说明，在绝热条件下减小磁场（$\Delta H < 0$），磁介质的温度将降低（$\Delta T < 0$），这个效应称为绝热去磁致冷。

如果磁介质的体积变化不能忽略，磁介质的热力学基本方程

$$dU = TdS - pdV + \mu_0 Hdm$$

吉布斯函数为 $G = U - TS + pV - \mu_0 Hm$

$$dG = -SdT + Vdp - \mu_0 mdH$$

比较 $dG = \frac{\partial G}{\partial T}dT + \frac{\partial G}{\partial p}dp + \frac{\partial G}{\partial H}dH$

由完整微分条件 $\frac{\partial^2 G}{\partial p \partial H} = \frac{\partial^2 G}{\partial H \partial p}$

得磁介质的麦氏关系 $\left(\frac{\partial V}{\partial H}\right)_{T,p} = -\mu_0 \left(\frac{\partial m}{\partial p}\right)_{T,H}$

$$\left(\frac{\partial V}{\partial H}\right)_{T,p} = -\mu_0\left(\frac{\partial m}{\partial p}\right)_{T,H}$$

磁致伸缩效应　　　　压磁效应

左方偏导数给出在保持温度和压强不变时体积随磁场的变化率，称为磁致伸缩效应；右方偏导数给出在保持温度和磁场不变时介质磁矩随压强的变化率，称为压磁效应。上式给出了磁致伸缩效应和压磁效应之间的关系。

$$đW = -\mu_0 m dH \qquad (2.7.19)$$

它不但包含当外磁场改变dH时，为使样品磁矩发生改变所做的功，而且包含样品在外磁场中势能的改变。