第三章　热力学函数

3.1　引言

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3.1 引言

热力学第零、第一和第二定律(分别给出了T, U, S):

$$
\begin{aligned}
dU &= đQ - đW \\
&= T d_e S - đW = T(dS - d_i S) - đW \\
&= T dS - đW - T d_i S \\
&= T dS - \sum_i y_i dX_i \\
&= T dS - p dV
\end{aligned}
$$

$$dU \le TdS - \sum_i y_i \, dX_i$$

可逆元过程

pV 系统中可逆元过程

- 有了热力学第零、一、二定律之后，热力学体系已经自洽和完整，可以只用系统参量描述系统过程，而不必借助外界参数。

原始参量：力学参量P、几何参量V、电磁学参量、化学参量

热力学参量：温度T、内能U，熵S 、焓H

3.1 引言

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\begin{aligned}
dU &= đQ - đW \\
&= Td_eS - đW = T(dS - d_iS) - đW \\
&= TdS - đW - Td_iS \\
&= TdS - \sum_i y_i dX_i \\
&= TdS - pdV
\end{aligned}
$$

$$dU \le TdS - \sum_i y_i \, dX_i$$

可逆元过程

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- 有了热力学第零、一、二定律之后，热力学体系已经自洽和完整，可以只用系统参量描述系统过程，而不必借助外界参数。

高级参量：内能$U(T,V) = U(p,V) \ldots$、熵S、焓H

选择以高级参量为自变量，更多的选择可以简化描述和计算：$U(S,V)$

$U(S,V)$对绝热膨胀过程非常好用，但对等压、等温过程就很不方便。

3.2 Legendre 变换

- 某个函数里包含了系统的信息

  其他物理量通常是该函数的某个偏微分

  例如：哈密顿量 $\boldsymbol{H}(\boldsymbol{r},\ \boldsymbol{p})$包含了$\boldsymbol{r}$和 $\boldsymbol{p}$ 随时间的改变

$$\boldsymbol{v} = \dot{\boldsymbol{r}} = \partial_{\boldsymbol{p}} H, \quad \boldsymbol{F} = \dot{\boldsymbol{p}} = -\partial_{\boldsymbol{r}} H$$

函数 $f(x, \cdots)$，x 和 $y = \partial_x f(x, \cdots)$ 一般称为对偶参量

$$\boldsymbol{v} = \dot{\boldsymbol{r}} = \partial_{\boldsymbol{p}} H, \quad \boldsymbol{F} = \dot{\boldsymbol{p}} = -\partial_{\boldsymbol{r}} H$$

3.2 Legendre 变换

使用对偶参量为自变量时，应该如何改变函数形式，使得函数里包含的信息保持不变？

- Legendre变换

$$y = y(x) = \partial_x f(x) \xrightarrow{\text{反解}} x = x(y)$$

$f^*(y) = f(x(y))$ 最简单，但是丢失信息

$$f(x) = ax^2 + bx + c \qquad y = \partial_x f = 2ax + b \qquad \Rightarrow x = \frac{y-b}{2a}$$

$$f^*(y) = a\left(\frac{y-b}{2a}\right)^2 + b\frac{y-b}{2a} + c = \frac{y^2}{4a} - \frac{b^2-4ac}{4a}$$

$$x = \partial_y f^* = \frac{y}{2a}$$

$$\boxed{\tilde{f}(y) = f^*(y) - xy} = -\frac{y^2-2by}{4a} - \frac{b^2-4ac}{4a}$$

$$x = -\partial_y \tilde{f}(y) = \frac{y-b}{2a} \qquad ☞ f(x) = \tilde{\tilde{f}}$$

注：
实现切线斜率和截距的一一映射。

3.2 Legendre 变换

- 经典力学里的Legendre 变换

  拉格朗日表述和哈密顿表述的转化：

$$H = H(\boldsymbol{r}, \boldsymbol{p})$$

$$\boldsymbol{v} = \dot{\boldsymbol{r}} = \partial_{\boldsymbol{p}} H(\boldsymbol{r}, \boldsymbol{p}) \qquad \boldsymbol{F} = \dot{\boldsymbol{p}} = -\partial_{\boldsymbol{r}} H$$

$$L = L(\boldsymbol{r}, \boldsymbol{v}) = \boldsymbol{p} \cdot \boldsymbol{v} - H$$

$$\boldsymbol{p} = \partial_{\boldsymbol{v}} L \qquad \dot{\boldsymbol{v}} = \partial_{\boldsymbol{r}} L$$

- ✓ 哈密顿描述和拉格朗日描述二者完全等价
- ✓ 经典力学里的Legendre 变换和热力学里的Legendre变换相差一个负号

3.2 Legendre 变换

- 多变量Legendre 变换

$$L = L(X_1, X_2, \cdots) \qquad dL = y_1 dX_1 + y_2 dX_2 + \cdots$$

$$y_1 = y_1(X_1, X_2, \cdots) = \left(\frac{\partial L}{\partial X_1}\right)_{X_2, X_3, \cdots}$$

$$y_2 = y_2(X_1, X_2, \cdots,) = \left(\frac{\partial L}{\partial X_2}\right)_{X_1, X_3, \cdots}$$

以 $y_1, X_2, X_3, \cdots$ 为自变量 $\xrightarrow{\text{反解}}$ $X_1 = X_1(y_1, X_2, X_3, \cdots)$

$$\begin{aligned}\tilde{L} = \tilde{L}(y_1, X_2, \cdots) &= L(X_1, X_2, \cdots) - X_1 y_1 \\ &= L(X_1(y_1, X_2, \cdots), X_2, \cdots) - X_1(y_1, X_2, \cdots) y_1\end{aligned}$$

$$\begin{aligned}d\tilde{L} &= dL - d(X_1 y_1) = y_1 dX_1 + y_2 dX_2 + \cdots - y_1 dX_1 - X_1 dy_1 \\ &= -X_1 dy_1 + y_2 dX_2 + \cdots\end{aligned}$$

$$X_1 = X_1(y_1, X_2, \cdots) = -\left(\frac{\partial \tilde{L}}{\partial y_1}\right)_{X_2, X_3, \cdots}$$

$$y_2 = y_2(y_1, X_2, \cdots) = \left(\frac{\partial \tilde{L}}{\partial X_2}\right)_{y_1, X_3, \cdots}$$

3.2 Legendre 变换

- 多参量变换

$$\tilde{L}(y_1, y_2, X_3, \cdots) \qquad d\tilde{L} = -X_1 dy_1 - X_2 dy_2 + y_3 dX_3 + \cdots$$

$$\tilde{L}(y_1, X_2, y_3, \cdots) \qquad d\tilde{L} = -X_1 dy_1 + y_2 dX_2 - X_3 dy_3 + \cdots$$

$$\tilde{L}(X_1, y_2, X_3, \cdots) \qquad d\tilde{L} = y_1 dX_1 - X_2 dy_2 + y_3 dX_3 + \cdots$$

$$\tilde{L}(y_1, y_2, y_3, \cdots) \qquad d\tilde{L} = -X_1 dy_1 - X_2 dy_2 - X_3 dy_3 + \cdots$$

- 对同一组对偶参量，做两次Legendre 变换变回原函数

$$\tilde{\tilde{L}} = L$$ Legendre 变换保持函数信息不变

3.3 热力学函数

热力学第零、第一和第二定律(分别给出了T, U, S):

$$dU = đQ - đW$$

$$= Td_eS - đW = T(dS - d_iS) - đW$$

$$= TdS - đW - Td_iS$$

$$dU = TdS - \sum_i y_i\, dX_i$$

$$= TdS - \sum_i y_i dX_i$$ 可逆元过程

$$= TdS - pdV$$ pV 系统中可逆元过程

- $U = U(S,V)$ 通过热力学定律，获得 $dU = TdS - pdV$。
- 函数$U = U(S,V)$ 里包含了体系的所有热力学信息。
- 特性函数方程：

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

3.3 热力学函数

特性函数

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

焓 $H = H(S,p) = U + pV$ $\qquad dH = TdS + Vdp$

自由能 $F = F(T,V) = U - TS$ $\qquad dF = -SdT - pdV$

Gibbs 自由能 $G = G(T,p) = U - TS + pV$ $\qquad dG = -SdT + Vdp$

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

记忆方法：$dU = TdS - pdV \xRightarrow[\text{S,V 为自变量}]{\text{全微分表达式}} U = U(S,V)$

$$dF = d(U - TS) = dU - d(TS) = TdS - pdV - TdS - SdT$$

$$= -SdT - pdV \xRightarrow[\text{以 T，V 为自变量}]{\text{全微分表达式}} F = F(T,V)$$

3.3 热力学函数

自由能

自由能/Helmholtz 自由能，理论上易得。

$$F = F(T,V) = U - TS \qquad dF = -SdT - pdV$$

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

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

$$C_{proc} = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}\bigg|_{proc} = \lim_{\Delta T \to 0} \frac{T\Delta S}{\Delta T}\bigg|_{proc} = T\left(\frac{\partial S}{\partial T}\right)_{proc}$$ 热容

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$ 等容热容 $= \left(\frac{\partial U}{\partial T}\right)_V$

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

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

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

3.3 热力学函数

Gibbs 自由能

Gibbs 自由能，实验上常用。

$$G = G(T,p) = U - TS + pV = F + pV \qquad dG = -SdT + Vdp$$

$$V = V(T,p) = \left(\frac{\partial G}{\partial p}\right)_T$$ 状态方程

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

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$ 等压热容

3.3 热力学函数

特性函数

- 选取特定的自变量，特征函数就确定下来了。

  $U(S,V)$，$H(S,p)$，$F(T,V)$，$G(T,V)$

- 除此之外还有

$$dU = TdS - pdV \qquad \Rightarrow$$

$$dS = \frac{dU}{T} + \frac{p}{T}dV \qquad S = S(U,V)$$

$$d\ \ln Z = d(S - U/T) = -Ud\frac{1}{T} + \frac{p}{T}dV \qquad Z = Z(\frac{1}{T}, V)$$

- 选好一组自变量，只有相应特性函数才包含所有信息：以(T,V)为自变量时，特性函数$F(T,V)$包含所有信息，但是$U(T,V)$则非如此

- 所有特性函数包含信息相同，选取哪个凭个人偏好和方便选取任何一个特性得到的结果都相同，可以互相转换

3.4 Jacobi 行列式

- 在计算热力学量以及它们之间的关系时，经常会涉及变量变换时偏微分之间的关系。这些关系可以用Jacobi 行列式计算。

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} u(x,y) \\ v(x,y) \end{pmatrix}$$

$$\begin{pmatrix} du \\ dv \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy \\ \left(\frac{\partial v}{\partial x}\right)_y dx + \left(\frac{\partial v}{\partial y}\right)_x dy \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix} = J\begin{pmatrix} uv \\ xy \end{pmatrix}\begin{pmatrix} dx \\ dy \end{pmatrix}$$

$$J\begin{pmatrix} uv \\ xy \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix}$$

$$\frac{\partial(uv)}{\partial(xy)} = \left|J\begin{pmatrix} uv \\ xy \end{pmatrix}\right| = \left|\begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix}\right|$$

$$= \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial v}{\partial y}\right)_x - \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y$$

3.4 Jacobi 行列式

- 偏微分用Jacobi 行列式表示

$$\left(\frac{\partial u}{\partial x}\right)_y=\frac{\partial(uy)}{\partial(xy)}=\left|\begin{pmatrix}\left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x\\ \left(\frac{\partial y}{\partial x}\right)_y & \left(\frac{\partial y}{\partial y}\right)_x\end{pmatrix}\right|=\left|\begin{pmatrix}\left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x\\ 0 & 1\end{pmatrix}\right|$$

- 互换奇数次行/列，行列式变号

$$\frac{\partial(uv)}{\partial(xy)}=-\frac{\partial(vu)}{\partial(xy)}=-\frac{\partial(uv)}{\partial(yx)}=\frac{\partial(vu)}{\partial(yx)}$$

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

3.4 Jacobi 行列式

➢ 矩阵乘积的行列式= 行列式的乘积

$$\begin{pmatrix} u = u(x,y) \\ v = v(x,y) \end{pmatrix} \qquad \begin{pmatrix} s = s(u,v) = s(u(x,y),v(x,y)) = s(x,y) \\ t = t(u,v) = t(u(x,y),v(x,y)) = t(x,y) \end{pmatrix}$$

$$\begin{pmatrix} ds \\ dt \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial s}{\partial u}\right)_v & \left(\frac{\partial s}{\partial v}\right)_u \\ \left(\frac{\partial t}{\partial u}\right)_v & \left(\frac{\partial t}{\partial v}\right)_u \end{pmatrix} \begin{pmatrix} du \\ dv \end{pmatrix}$$

$$= \begin{pmatrix} \left(\frac{\partial s}{\partial u}\right)_v & \left(\frac{\partial s}{\partial v}\right)_u \\ \left(\frac{\partial t}{\partial u}\right)_v & \left(\frac{\partial t}{\partial v}\right)_u \end{pmatrix} \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix}$$

$$= \begin{pmatrix} \left(\frac{\partial s}{\partial x}\right)_y & \left(\frac{\partial s}{\partial y}\right)_x \\ \left(\frac{\partial t}{\partial x}\right)_y & \left(\frac{\partial t}{\partial y}\right)_x \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix}$$

定义上

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

很像分数运算

3.4 Jacobi 行列式

- 逆矩阵的行列式= 行列式的逆

$$\begin{pmatrix} u = u(x,y) \\ v = v(x,y) \end{pmatrix} \xrightarrow{\text{逆方程}} \begin{pmatrix} x = x(u,v) \\ y = y(u,v) \end{pmatrix}$$

$$\begin{pmatrix} dx \\ dy \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix}^{-1} \begin{pmatrix} du \\ dv \end{pmatrix}$$

$$= \begin{pmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{pmatrix} \begin{pmatrix} du \\ dv \end{pmatrix}$$ 定义上

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

3.4 Jacobi 行列式

- 对多个参量同样成立

- $$\left(\frac{\partial u}{\partial x}\right)_{y,z,\cdots} = \frac{\partial(u,y,z,\cdots)}{\partial(x,y,z,\cdots)}$$

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

  $\cdots$

- $$\frac{\partial(u,v,w,\cdots)}{\partial(p,q,r,\cdots)}\frac{\partial(p,q,r,\cdots)}{\partial(x,y,z,\cdots)} = \frac{\partial(u,v,w,\cdots)}{\partial(x,y,z,\cdots)}$$

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

3.4 Jacobi 行列式

微分关系

- $$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial(x,z)}{\partial(y,z)} = 1/\frac{\partial(y,z)}{\partial(x,z)}$$

$$= 1/\left(\frac{\partial y}{\partial x}\right)_z$$

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

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

$$= (-1)^3\frac{\partial(z,x)}{\partial(y,z)}\frac{\partial(x,y)}{\partial(z,x)}\frac{\partial(y,z)}{\partial(x,y)} = -\frac{\partial(z,x)}{\partial(y,z)}\frac{\partial(y,z)}{\partial(z,x)}$$

$$= -\frac{\partial(z,x)}{\partial(z,x)} = -1$$

3.5 Maxwell 关系

光滑函数二阶偏微分和微分次序无关) $\Longrightarrow$ **Maxwell 关系**

$$\frac{\partial^2 f}{\partial x \partial y} = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \frac{\partial^2 f}{\partial y \partial x} = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x$$

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

$$\left(\frac{\partial T}{\partial V}\right)_S = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

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

$$\frac{\partial(T,S)}{\partial(V,S)} = -\frac{\partial(p,V)}{\partial(S,V)} = \frac{\partial(p,V)}{\partial(V,S)}$$

$$1 = \frac{\partial(T,S)}{\partial(V,S)} \Big/ \frac{\partial(p,V)}{\partial(V,S)} = \frac{\partial(T,S)}{\partial(V,S)} \frac{\partial(V,S)}{\partial(p,V)} = \frac{\partial(T,S)}{\partial(p,V)}$$

3.5 Maxwell 关系

光滑函数二阶偏微分和微分次序无关) $\Longrightarrow$ **Maxwell 关系**

$$\frac{\partial^2 f}{\partial x \partial y} = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \frac{\partial^2 f}{\partial y \partial x} = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x$$

- $U = U(S, V)$ $\quad dU = TdS - pdV \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
- $H = H(S, p)$ $\quad dH = TdS + Vdp \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
- $F = F(T, V)$ $\quad dF = -SdT - pdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
- $G = G(T, p)$ $\quad dG = -SdT + Vdp \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

☞ 可统一标记为 $\frac{\partial(T, S)}{\partial(p, V)} = 1$

注：能量守恒

3.5 Maxwell 关系

更多参量 $dU = TdS - \text{đ}W = TdS - y_1 dX_1 - y_2 dX_2 - \cdots$

$$U = U(S, X_1, X_2, \cdots) \Rightarrow F = U - TS = F(T, X_1, X_2, \cdots)$$

$$dF = -SdT - \text{đ}W = -SdT - y_1 dX_1 - y_2 dX_2 - \cdots$$

$$\left(\frac{\partial S}{\partial X_1}\right)_{T, X_2, \cdots} = \left(\frac{\partial y_1}{\partial T}\right)_{X_1, X_2, \cdots}$$

$$\left(\frac{\partial S}{\partial X_2}\right)_{T, X_1, \cdots} = \left(\frac{\partial y_2}{\partial T}\right)_{X_1, X_2, \cdots}$$

$$\left(\frac{\partial y_1}{\partial X_2}\right)_{T, X_1, \cdots} = \left(\frac{\partial y_2}{\partial X_1}\right)_{T, X_2, \cdots}$$

3.5 Maxwell 关系

如何记住Maxwell 关系

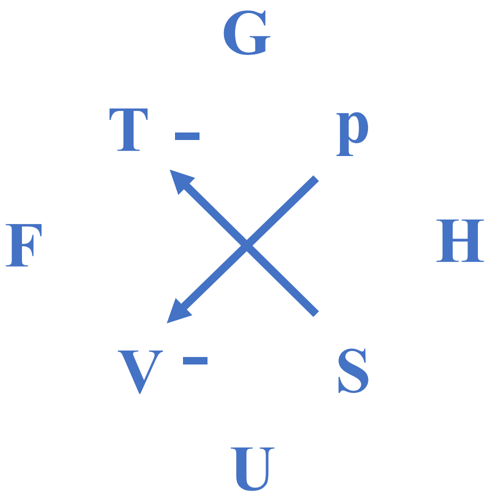
- 记住特性函数的定义以及$dU = TdS - pdV$即可
- **G**ood **P**hysicists **H**ave **S**tudied **U**nder **V**ery **F**ine **T**eachers.

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

$$dH = TdS + Vdp \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$dF = -SdT - pdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$dG = -SdT + Vdp \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$



- TdS是热学效应，$-pdV$是力学效应，对于磁/电有：

$$dU = TdS + HdM; dU = TdS + EdP$$

3.5 Maxwell 关系

热容之间的关系

$$dU = đQ - đW = TdS - đW = TdS - y_1 dX_1 - y_2 dX_2 \cdots$$

$$C_{proc} = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}\bigg|_{proc} = \lim_{\Delta T \to} \frac{T\Delta S}{\Delta T}\bigg|_{proc}$$

$$= T\left(\frac{\partial S}{\partial T}\right)_{proc}$$

$$= \lim_{\Delta T \to 0} \frac{\Delta U + \Delta W}{\Delta T}\bigg|_{proc}$$

$$= \left(\frac{\partial U}{\partial T}\right)_{proc} + y_1\left(\frac{\partial X_1}{\partial T}\right)_{proc} + y_2\left(\frac{\partial X_2}{\partial T}\right)_{proc} + \cdots$$

- ✓ 有无穷多热容，不同过程有不同的热容
- ✓ 同一种热容是一个状态函数

3.5 Maxwell 关系

热容之间的关系

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

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

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

$$= \boxed{T\frac{\partial(S,V)}{\partial(T,V)}}\frac{\partial(S,p)}{\partial(S,V)}\frac{\partial(T,V)}{\partial(T,p)} = \boxed{T\frac{\partial(S,V)}{\partial(T,V)}}\frac{\partial(T,V)}{\partial(T,p)}\Big/\frac{\partial(S,V)}{\partial(S,p)}$$

$$\boxed{= C_V\left(\frac{\partial V}{\partial p}\right)_T\Big/\left(\frac{\partial V}{\partial p}\right)_S} = C_V\frac{\kappa_T}{\kappa_S}$$

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

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

等温压缩系数

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

绝热压缩系数

3.5 Maxwell 关系

热容之间的关系

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

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

$$dG = -SdT + Vdp \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

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

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

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

$$= C_p + T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T = C_p - TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]^2 \Big/ \left[-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right]$$

☞ $C_p - C_V = TV\alpha^2/\kappa_T$

3.5 Maxwell 关系

热容之间的关系

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

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

$$\Rightarrow \frac{TV\alpha^2}{\kappa_T C_V} = \frac{C_p}{C_V} - 1 = \frac{\kappa_T}{\kappa_S} - 1 = \frac{\kappa_T - \kappa_S}{\kappa_S}$$

$$C_V = \frac{TV\alpha^2 \kappa_S}{\kappa_T(\kappa_T - \kappa_S)}$$

$$C_p = \frac{TV\alpha^2}{\kappa_T - \kappa_S}$$

- 原则上可以用这些公式通过测量κ_T、κ_S和α 来得到热容，实际上很困难。

3.5 Maxwell 关系

热容测量

以 T,p 为自变量，状态方程 $V(T,p)$

$$dG = -SdT + Vdp \qquad \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

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

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left[\frac{\partial}{\partial p}T\left(\frac{\partial S}{\partial T}\right)_p\right]_T = T\frac{\partial^2 S}{\partial p\partial T} = T\frac{\partial^2 S}{\partial T\partial p}$$

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

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

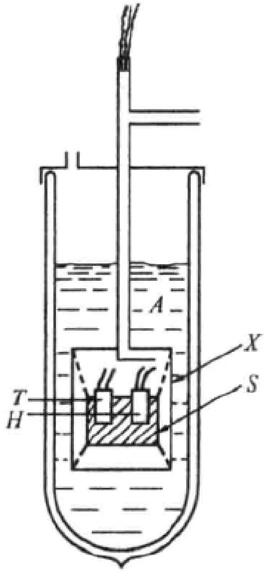


图 4.10　比热容测量装置

样品(S)用尼龙线吊在真空室(X)中，

H 为加热器，T 为温度计

$$C_p(T,p) = C_p(T,p_0) + \int_{p_0}^{p}\left(\frac{\partial C_p}{\partial p}\right)_T dp = C_p(T,p_0) - \int_{p_0}^{p} T\frac{\partial^2 V}{\partial T^2}dp$$

- 可利用热力学关系，减少实验测量次数：测得某个压强p_0下的热容$C_p(T,p_0)$，加上状态方程$V = V(T,p)$, 即可得到所有压强下热容$C_p(T,p)$
- 工业上称为million dollar formula

3.5 Maxwell 关系

特性函数的测量

特性函数如$G=G(T,p)$无法直接测量，实验上能测的是状态方程$V=V(T,p)$和比热 $C_p=C_p(T,p)$，可利用这些数据得到特性函数

$$G=G(T,p) \qquad dG=-SdT+Vdp \qquad \Leftarrow$$ 有 V 和 S，可积分得 G

$$V=V(T,p) \qquad \Leftarrow$$ 状态方程，可从实验测得

$$S=S(T,p)=? \quad \Leftarrow \quad dS=\left(\frac{\partial S}{\partial T}\right)_p dT+\left(\frac{\partial S}{\partial p}\right)_T dp=\frac{C_p}{T}dT-\left(\frac{\partial V}{\partial T}\right)_p dp$$

从 S直接计算G 要积分两次，为了简化计算，我们先求焓H

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

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

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

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