1. 求证：$\frac{K_S}{K_T}=\frac{C_V}{C_P}$. $K_S=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ $K_T=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

证明：$\frac{K_S}{K_T}=\frac{(\partial V/\partial P)_S}{(\partial V/\partial P)_T}=\frac{\partial(V,S)}{\partial(P,S)}\Big/\frac{\partial(V,T)}{\partial(P,T)}$

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

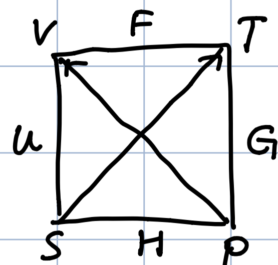
$dS=\frac{C_V dT}{T}$ $$=\frac{\frac{1}{T}C_V}{\frac{1}{T}C_P}$$ $\left(\frac{\partial S}{\partial T}\right)_V=\frac{C_V}{T}$ $\left(\frac{\partial S}{\partial T}\right)_P=\frac{C_P}{T}$

2. 求证：$C_P-C_V=-T\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T}$

证明：$C_P=T\left(\frac{\partial S}{\partial T}\right)_P=T\frac{\partial(S,P)}{\partial(T,P)}=T\frac{\frac{\partial(S,P)}{\partial(T,V)}}{\frac{\partial(T,P)}{\partial(T,V)}}$

$$\frac{\partial(S,P)}{\partial(T,V)}=\begin{vmatrix}\frac{\partial S}{\partial T} & \frac{\partial P}{\partial T}\\ \frac{\partial S}{\partial V} & \frac{\partial P}{\partial V}\end{vmatrix}=\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial P}{\partial V}\right)_T-\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$$

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



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

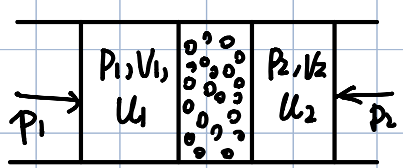
$$\Rightarrow C_P=T\cdot\frac{\frac{C_V}{T}\left(\frac{\partial P}{\partial V}\right)_T-\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}=C_V-T\cdot\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}$$

$$\Rightarrow C_P-C_V=-T\frac{\left(\frac{\partial P}{\partial T}\right)^2}{\left(\frac{\partial P}{\partial V}\right)_T}\xlongequal[\text{gas}]{\text{ideal}}nR$$ $PV=nRT$

3. $\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial S}{\partial V}\right)_T-P=T\left(\frac{\partial P}{\partial T}\right)_V-P$. $dU=TdS-PdV$

$\left(\frac{\partial H}{\partial P}\right)_T=T\left(\frac{\partial S}{\partial P}\right)_T+V=-T\left(\frac{\partial V}{\partial T}\right)_P+V$ $dH=-TdS-VdP$

气体的节流过程（绝热）



$P_1>P_2$

焦耳—汤姆逊效应

气体对外做功 $-P_1V_1+P_2V_2$

外界对气体做功 $P_1V_1-P_2V_2=U_2-U_1$

$\Rightarrow P_1V_1+U_1=P_2V_2+U_2$

$\Rightarrow H_1=H_2$ 等焓.

焦耳—汤姆逊系数 $\mu=\left(\frac{\partial T}{\partial P}\right)_H$

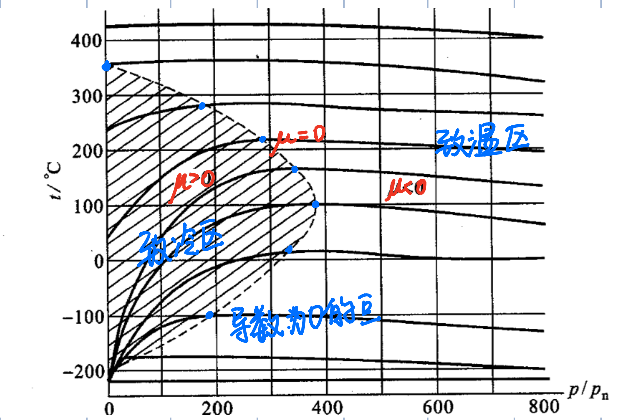
$$H=H(T,p) \quad f(H,T,p)=0$$

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

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

$$=\frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p-P\right] \xlongequal[\text{gas}]{\text{ideal}} 0$$

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



昂尼斯方程

理想气体 $P=\frac{nRT}{V}$ Van der Walls $p=\frac{nRT}{V-nb}-\frac{V^2}{a^2n^2}$

$$=\frac{nRT}{V}\left(1+\frac{nb}{V}+\frac{(nb)^2}{V^2}\right)-\frac{V^2}{a^2n^2}$$

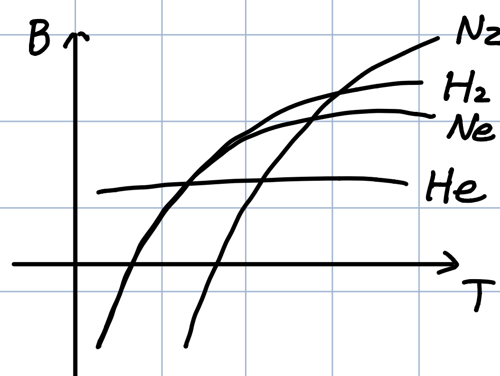
$$p=\frac{nRT}{V}\left[1+\frac{n}{V}B(T)+O\left(\frac{1}{V^2}\right)\right]$$

0阶: $\frac{n}{V}=\frac{P}{RT}$

1阶 $\left(\frac{n}{V}B\ll 1\right)$ $\underline{p=\frac{nRT}{V}\left(1+\frac{P}{RT}B(T)\right)}$

$$V=\frac{nRT}{P}\left(1+\frac{P}{RT}B(T)\right)$$

$$=n\left(\frac{RT}{P}+B(T)\right)$$



$$\Rightarrow \alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \approx \frac{1}{V}\left(\frac{nR}{P}+n\frac{dB}{dT}\right)$$

$$\Rightarrow \mu=\frac{V}{C_p}(T\alpha-1)=\frac{1}{C_p}\left(T\left(\frac{nR}{P}+n\frac{dB}{dT}\right)-V\right)$$

$$=\frac{n}{C_p}\left[T\frac{dB}{dT}+\underline{\frac{TR}{P}-\frac{V}{n}}\right]$$

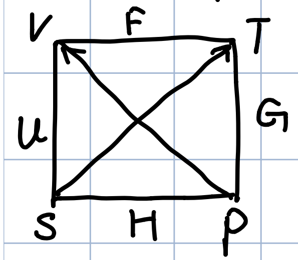
$$=\frac{n}{C_p}\left(T\frac{dB}{dT}-B\right)$$

低温时 $\frac{dB}{dT}>0$, $B<0$, $\mu>0 \Rightarrow$ 致冷

高温时 若 $B>T\frac{dB}{dT}$, $\mu<0 \Rightarrow$ 致温

理想气体绝热膨胀 $dS=0$

$S=S(T,p)$ $\quad dS=\left(\frac{\partial S}{\partial T}\right)_p dT+\left(\frac{\partial S}{\partial p}\right)_T dp=0$



$$\left(\frac{\partial T}{\partial p}\right)_S=\frac{\partial(T,S)}{\partial(p,S)}=\frac{\frac{\partial(T,S)}{\partial(T,p)}}{\frac{\partial(p,S)}{\partial(T,p)}}=\frac{\left(\frac{\partial S}{\partial p}\right)_T}{-\left(\frac{\partial S}{\partial T}\right)_p}=\frac{\left(\frac{\partial V}{\partial T}\right)_p}{C_p/T}=\frac{\alpha TV}{C_p}>0$$

$p\downarrow \rightarrow T\downarrow$ 致冷过程

基本热力学函数

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

(T,V) $\quad p=p(T,V)$

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

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

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

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

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

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

Homework: 2.6 2.9