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习题2.1 解：由已知，$p=f(V)T$

由 $dF=-SdT-pdV$

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

代入 $p=f(V)T$ 解得：

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

可知 $\left(\frac{\partial S}{\partial V}\right)_T>0$

温度不变，熵随体积增大而增加

2.2 解：由已知，~~$\left(\frac{\partial p}{\partial V}\right)_T$~~

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

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

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

又由 $p=f(V)T$

可得 $\left(\frac{\partial U}{\partial V}\right)_T=0$

即物质内能与体积无关

2.3 解：(a) $dH=TdS+Vdp$

令 $dH=0$，

得 $\left(\frac{\partial S}{\partial p}\right)_H=-\frac{V}{T}<0$

(b) $dU=TdS-pdV$

令 $dU=0$

得 $\left(\frac{\partial S}{\partial V}\right)_U=\frac{p}{T}>0$

2.4 解：$U(T,p)=U(T,V(T,p))$

对其求偏导，有 $\left(\frac{\partial U}{\partial p}\right)_T=\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T$

令 $\left(\frac{\partial U}{\partial V}\right)_T=0$，

可得 $\left(\frac{\partial U}{\partial p}\right)_T=0$

证毕

2.5. 解：要证命题，即证 $\left(\frac{\partial S}{\partial V}\right)_p \propto \left(\frac{\partial T}{\partial V}\right)_p$

~~即有~~ 由 $S(p,V)=S(p,T(p,V))$

两边求偏导，有 $\left(\frac{\partial S}{\partial V}\right)_p=\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p=\frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p$

$\because C_p>0,\ T>0$ 即 $\frac{C_p}{T}>0$

$\therefore \left(\frac{\partial S}{\partial V}\right)_p \propto \left(\frac{\partial T}{\partial V}\right)_p$

2.7. 解：$\left(\frac{\partial T}{\partial p}\right)_S-\left(\frac{\partial T}{\partial p}\right)_H>0 \Leftrightarrow \left(\frac{\partial T}{\partial p}\right)_S>\left(\frac{\partial T}{\partial p}\right)_H$

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

$\Rightarrow$ ~~解得~~ $\left(\frac{\partial S}{\partial T}\right)_p dT=-\left(\frac{\partial S}{\partial p}\right)_T dp$

$$\left(\frac{\partial T}{\partial p}\right)_S=-\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}=\frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p} \quad ①$$

由 $dH(T,p)=\left(\frac{\partial H}{\partial T}\right)_p dT+\left(\frac{\partial H}{\partial p}\right)_T dp=0$

同理，$$\left(\frac{\partial T}{\partial p}\right)_H=\frac{T\left(\frac{\partial V}{\partial T}\right)_p-V}{C_p} \quad ②$$

对比上式①②可知：式① > 式②

即 $\left(\frac{\partial T}{\partial p}\right)_S>\left(\frac{\partial T}{\partial p}\right)_H$ 即证得原式 $\left(\frac{\partial T}{\partial p}\right)_S-\left(\frac{\partial T}{\partial p}\right)_H$

习题2.9. 证明：由 $C_V=\left(\frac{\partial U}{\partial T}\right)_V=T\left(\frac{\partial S}{\partial T}\right)_V$

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

同理，有 $\left(\frac{\partial C_p}{\partial p}\right)_T=T\left(\frac{\partial^2 V}{\partial T^2}\right)$

对两式两边积分，有

$$C_V=C_V^0+T\int_{V_0}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV$$

$$C_p=C_p^0-T\int_{p_0}^{p}\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp$$

理想气体 $pV=RT$

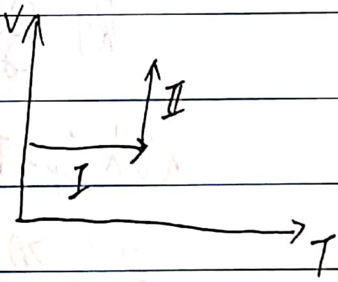
可得：$C_V=C_V^0+f(T)=f(T)$

同理，$C_p=g(T)$

2.11. 证明：对理想气体，有

$$\begin{cases} du=C_V dT,\ u=u(T) \\ f=u-Ts,\ df=du-Tds-sdT \end{cases}$$

如右图选取积分路径，



I中，$s_1=\int\frac{du}{T}=\int\frac{C_V dT}{T}$

$u-u_0=C_V dT$，同理 $s-s_0=\int\frac{C_V dT}{T}$

得 $\Delta f_1=u-Ts=\int C_V dT+u_0-T\int\frac{C_V dT}{T}-Ts_0$

II中，有 $\Delta u=0$，由热力学第一定律，

$$\Delta Q=\int p dV=RT\int_{V_0}^{V}\frac{dV}{V}=RT\ln\frac{V}{V_0}$$

$$f=\Delta u-Ts=-\Delta Q=-RT\ln\frac{V}{V_0}$$

综上，$F_m=f=-T\int\frac{dT}{T}dT-RT\ln V_m-TS_{m0}+U_{m0}+\int C_{V,m}dT$

$$=-T\int\frac{dT}{T^2}\int C_{V,m}dT+U_{m0}-TS_{m0}-RT\ln V_m$$

习题三.4 证明：由已知，$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$

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

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

解得：
$$\begin{cases}\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial p}{\partial V}\right)_S \\ \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial p}{\partial S}\right)_V\left(\frac{\partial S}{\partial T}\right)_T\end{cases}$$

代入麦氏关系，解得：

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

$\Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V \Leftrightarrow \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0$

即 $\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial V}\right)_S + C < 0$，$C$为一正值

则 $\left(\frac{\partial p}{\partial V}\right)_S < 0$

代入 $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$，可得 $C_p = \left(\frac{\partial p}{\partial V}\right)_S\left(\frac{\partial V}{\partial p}\right)_T \cdot C_V$

由 $C_V > 0$，$\left(\frac{\partial p}{\partial V}\right)_S\left(\frac{\partial V}{\partial p}\right)_T > 0$

得 $C_p > 0$

习题三.6 解:

由 $\begin{cases} dG = -SdT + Vdp + \mu dn \\ p = p(V,T) \end{cases}$

解得: $dG = \left[-S + V\left(\frac{\partial p}{\partial T}\right)_V\right]_n dT + \left[V\left(\frac{\partial p}{\partial V}\right)_T\right]_n dV + \mu dn$

$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_{V,n} = -S + V\left(\frac{\partial p}{\partial T}\right)_V$

得 $\left(\frac{\partial G}{\partial V}\right)_{T,n} = V\left(\frac{\partial p}{\partial V}\right)_T$

同理, 解得 $\left(\frac{\partial G}{\partial n}\right)_{T,V} = \mu$

由上式得 $S = \left[V\left(\frac{\partial p}{\partial T}\right)_V\right]_n - \left(\frac{\partial G}{\partial T}\right)_{V,n}$

两边求偏导解得:

$\left(\frac{\partial S}{\partial n}\right)_{T,V} = -\left(\frac{\partial^2 G}{\partial T \partial n}\right)_V = -\left(\frac{\partial \mu}{\partial T}\right)_{V,n}$

证毕.

(2) 由已知, 同理可证

$\left(\frac{\partial V}{\partial n}\right)_{T,p} = \left(\frac{\partial^2 G}{\partial p \partial n}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_{T,n}$

习题三、7 证明:

$$\left(\frac{\partial U}{\partial n}\right)_{T,V} = \left(\frac{\partial F}{\partial n}\right)_{T,V} + T\left(\frac{\partial S}{\partial n}\right)_{T,V}$$

$$\because \mu = \left(\frac{\partial F}{\partial n}\right)_{T,V}$$

$$\therefore \left(\frac{\partial U}{\partial n}\right)_{T,V} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{V,n}$$

麦克斯韦关系推导

(1) $\begin{cases} H = G + Ts = U + pV = Ts + \mu n \\ dH = T\,ds + s\,dT + \mu\,dn + n\,d\mu = T\,ds + V\,dp + \mu\,dn \end{cases}$

解得：$s\,dT + n\,d\mu = V\,dp$

则 $\left(\frac{\partial T}{\partial p}\right)_{s,n} = \left(\frac{\partial V}{\partial s}\right)_{p,n}$

$\left(\frac{\partial T}{\partial n}\right)_{s,p} = \left(\frac{\partial \mu}{\partial s}\right)_{n,p}$

$\left(\frac{\partial \mu}{\partial p}\right)_{s,n} = \left(\frac{\partial V}{\partial n}\right)_{s,p}$

(2) $\begin{cases} F = G - pV = U - Ts = \mu n - pV \\ dF = -p\,dV - V\,dp + \mu\,dn + n\,d\mu = -s\,dT - p\,dV - \mu\,dn \end{cases}$

解得：$-V\,dp + n\,d\mu = -s\,dT$

则 $\left(\frac{\partial s}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V,n}$

$\left(\frac{\partial s}{\partial n}\right)_{T,n} = -\left(\frac{\partial \mu}{\partial T}\right)_{n,V}$

$\left(\frac{\partial \mu}{\partial V}\right)_{T,n} = -\left(\frac{\partial p}{\partial n}\right)_{T,V}$

(3) $\begin{cases} G = \mu n \\ dG = \mu\,dn + n\,d\mu = -s\,dT + V\,dp + \mu\,dn \end{cases}$

解得：$n\,d\mu = -s\,dT + V\,dp$

$\left(\frac{\partial s}{\partial p}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{p,n}$

$\left(\frac{\partial s}{\partial n}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{n,p}$

$\left(\frac{\partial \mu}{\partial p}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{T,p}$