1.2 热平衡定律(热0律):若A,B各与处于同一状态C达热平衡,若A,B热接触,两者亦热平衡

1.3 定压膨胀系数:$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$;**定容压力系数**:$\beta=\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$;**等温压缩系数**:$\kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

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

玻意耳定律:当T,n,$pV=C$; **阿伏伽德罗定律**:相同T,p下任何气体V_m均相同,$V_{m0}=22.4L/\mathrm{mol}(1\mathrm{atm},273\mathrm{K})$

理想气体物态方程:$pV=nRT$,$(R=8.3145\mathrm{J\cdot mol^{-1}\cdot K^{-1}})$; **非理想气体状态方程**:**范德瓦尔斯方程**:$(p+\frac{an^2}{V^2})(V-nb)=nRT$; **昂尼斯方程**:$p=\frac{nRT}{V}\left[1+\frac{n}{V}B(T)+\left(\frac{n}{V}\right)^2C(T)+\cdots\right]$,($B,C$–第2,3位力系数)

1.4 体积功:$dW=-pdV,W=-\int_{V_1}^{V_2}pdV$; **功的一般表达式**:$dW=\sum_{i=1}Y_idy_i$($Y_i$–广义力,$y_i$–广义坐标)

1.5 热力学第一定律:自然界一切物质都具有能量,能量有各种不同的形式,可以从一种形式转化为另一种形式,从一个物体传递到另一个物体,在传递和转化中能量的数量不变;$\Delta U=W+Q$或$dU=đW+đQ$

1.6 等容热容量:$C_V=\lim_{\Delta T\to 0}\left(\frac{\Delta Q}{\Delta T}\right)_V=\left(\frac{\partial U}{\partial T}\right)_V$; **等压热容量**:$C_p=\lim_{\Delta T\to 0}\left(\frac{\Delta Q}{\Delta T}\right)_p$

焓:$H=U+pV$;$C_p=\left(\frac{\partial H}{\partial T}\right)_p$ 对理想气体,$C_p-C_V=nR,C_V=\frac{nR}{\gamma-1}$,(**热容比**$\gamma=\frac{C_p}{C_V}$)

1.8 理想气体的绝热过程:$pV^\gamma=C_1,TV^{\gamma-1}=C_2,p^{\gamma-1}T^{-\gamma}=C_3$

1.10 热力学第二定律 开尔文表述:不可能从单一热源吸热使之完全变为有用功而不引起其他变化

克劳修斯表述:不可能把能量从低温物体传到高温物体而不引起其他变化

1.11 卡诺定理:所有工作在一定温度间的热机,以可逆热机效率最高,$\eta=1-\frac{Q_2}{Q_1}\le 1-\frac{T_2}{T_1}$(对可逆热机=,不可逆热机<)

1.14 熵变:$S_B-S_A=\int_A^B\frac{dQ}{T}$(沿可逆过程积分,不可逆过程的熵变可用相同初末态的可逆过程计算)

1.16 熵增加原理:系统经绝热过程从一状态到另一状态,其熵永不减少,若过程可逆,则熵保持不变,若不可逆,则熵增;**推论**:孤立系统内部任何自发过程总朝着熵增方向进行,当熵达最大,系统平衡 **1.18 自由能**:$F=U-TS$;**最大功原理**:等温过程中,系统对外做功不大于其自由能的减少,$-W\le F_A-F_B$;**自由能判据**:等温等容条件下,F永不增加,不可逆反应总朝$F\downarrow$的方向进行;**吉布斯函数**: $G=F+pV=U-TS+pV$;**吉布斯函数判据**:等温等压过程中,G永不增加,不可逆过程总朝$G\downarrow$的方向进行

2.1 热力学基本微分方程:$dU=TdS-pdV,H=TdS+Vdp,dF=-SdT-pdV,dG=-SdT+Vdp$

麦克斯韦关系:$\left(\frac{\partial U}{\partial S}\right)_V=T,\left(\frac{\partial U}{\partial V}\right)_S=-p\Rightarrow\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V$

$\left(\frac{\partial H}{\partial S}\right)_p=T,\left(\frac{\partial H}{\partial p}\right)_S=V\Rightarrow\left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_p$; $\left(\frac{\partial F}{\partial T}\right)_V=-S,\left(\frac{\partial F}{\partial V}\right)_T=-p\Rightarrow\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V$; $\left(\frac{\partial G}{\partial T}\right)_p=-S,\left(\frac{\partial G}{\partial p}\right)_T=V\Rightarrow\left(\frac{\partial S}{\partial p}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_p$

2.2 内能方程:$dU=T\left(\frac{\partial S}{\partial T}\right)_VdT+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV$;$C_V=T\left(\frac{\partial S}{\partial T}\right)_V,\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p$

焓方程:$dH=T\left(\frac{\partial S}{\partial T}\right)_pdT+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp\Rightarrow C_p=T\left(\frac{\partial S}{\partial T}\right)_p,\left(\frac{\partial H}{\partial p}\right)_T=V-T\left(\frac{\partial V}{\partial T}\right)_p$

定压与定容热容量之差:$C_p-C_V=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p=TVp\alpha\beta=\frac{VT\alpha^2}{\kappa_T}$

2.3 节流过程:气体由高压流至低压并达定常状态,为**等焓过程**; **焦汤系数**:$\mu=\left(\frac{\partial T}{\partial p}\right)_H=\frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p-V\right]=\frac{V}{C_p}(T\alpha-1)$; **绝热膨胀**:$\mu_S=\left(\frac{\partial T}{\partial p}\right)_S=\frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p=\frac{VT\alpha}{C_p}$

2.4 $dU=C_VdT+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV\Rightarrow U=\int\left\{C_VdT+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV\right\}+U_0$

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

$dH=C_pdT+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp\Rightarrow H=\int\left\{C_pdT+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp\right\}+H_0$

$dS=\frac{C_p}{T}dT-\left(\frac{\partial V}{\partial T}\right)_pdp\Rightarrow S=\int\left[\frac{C_p}{T}dT-\left(\frac{\partial V}{\partial T}\right)_pdp\right]+S_0$

计算要点:1.已知物态方程和C_V,C_p,可得U,S和H;2.由此得其他热力学函数;3.$C_V(T,V)=C_V(T,V_0)+T\int_{V_0}^{V}\left(\frac{\partial^2p}{\partial T^2}\right)_VdV,C_p(T,p)=C_p(T,p_0)-T\int_{p_0}^{p}\left(\frac{\partial^2V}{\partial T^2}\right)_pdp$

2.5 $F(T,V)$作特性函数,$S=-\left(\frac{\partial F}{\partial T}\right)_V,p=-\left(\frac{\partial F}{\partial V}\right)_T,U=F-T\left(\frac{\partial F}{\partial T}\right)_V$(**吉布斯-亥姆霍兹方程**),$H=U+pV,G=F+pV$ $G(T,p)$作特性函数,$S=-\left(\frac{\partial G}{\partial T}\right)_p,V=\left(\frac{\partial G}{\partial p}\right)_T,H=G-T\left(\frac{\partial G}{\partial T}\right)_p$(**吉布斯-亥姆霍兹方程**),$F=G-pV,U=G-pV+TS$

2.6 平衡辐射特性的热力学函数:**辐射压力和能量密度之间的关系**:$p=u/3$,**内能**:$U=aVT^4$,**熵**:$S=\frac{4}{3}aT^3V$,**自由能**:$F=-\frac{1}{3}aVT^4$,**焓**:$H=\frac{4}{3}aVT^4$,**吉布斯函数**:$G=F+pV=0$

斯特藩-玻尔兹曼定律:辐射通量密度$J=\sigma T^4$(斯特藩常数:$\sigma=5.67\times10^{-8}\mathrm{Wm^{-2}K^{-4}}$)

2.7 磁介质的热力学 $dW=\mu_0\mathcal{H}dm,p\to-\mu_0\mathcal{H},V\to m$

热力学基本方程:$dU=TdS+\mu_0\mathcal{H}dm,H=U-\mu_0\mathcal{H}m,dH=TdS-\mu_0md\mathcal{H},F=U-TS,dF=-SdT+\mu_0\mathcal{H}dm,G=F-\mu_0\mathcal{H}m=U-TS-\mu_0\mathcal{H}m,dG=-SdT-\mu_0md\mathcal{H}$ **麦氏关系**:$\left(\frac{\partial T}{\partial m}\right)_S=\mu_0\left(\frac{\partial\mathcal{H}}{\partial S}\right)_m,\left(\frac{\partial T}{\partial\mathcal{H}}\right)_S=-\mu_0\left(\frac{\partial m}{\partial S}\right)_{\mathcal{H}},\left(\frac{\partial S}{\partial m}\right)_T=-\mu_0\left(\frac{\partial\mathcal{H}}{\partial T}\right)_m,\left(\frac{\partial S}{\partial\mathcal{H}}\right)_T=\mu_0\left(\frac{\partial m}{\partial T}\right)_{\mathcal{H}}$

3.2 开系的热力学基本方程:$dU=TdS-pdV+\mu dn,\mu=\left(\frac{\partial U}{\partial n}\right)_{S,V}$;$dG=-SdT+Vdp+\mu dn$,其中**化学势**$\mu=\left(\frac{\partial G}{\partial n}\right)_{T,p}$,$G(T,p,n)=n\mu$;$dH=TdS+Vdp+\mu dn,\mu=\left(\frac{\partial H}{\partial n}\right)_{S,p}$;$dF=-SdT-pdV+\mu dn,\mu=\left(\frac{\partial F}{\partial n}\right)_{T,V}$; **巨热力学势**:$J(T,V,\mu)=F-\mu n=-pV$,**巨热力学势的微分**$dJ=-SdT-pdV-nd\mu$,以$J$为特性函数,$S=-\left(\frac{\partial J}{\partial T}\right)_{V,\mu},p=-\left(\frac{\partial J}{\partial V}\right)_{T,\mu},n=-\left(\frac{\partial J}{\partial\mu}\right)_{T,V}$

3.3 单元系的复相平衡条件:**热平衡条件**:$T^\alpha=T^\beta$;**力学平衡条件**:$p^\alpha=p^\beta$;**相平衡条件**:$\mu^\alpha=\mu^\beta$ **3.4 单元复相系的平衡性质 克拉珀龙方程**:沿相平衡曲线,$\frac{dp}{dT}=\frac{S_m^\beta-S_m^\alpha}{V_m^\beta-V_m^\alpha}=\frac{L}{T(V_m^\beta-V_m^\alpha)}$,**相变潜热**:$L=T(S_m^\beta-S_m^\alpha)$

4.8 热力学第三定律 能斯特定理:$\lim_{T\to0}(\Delta S)_T=0$; **热力学第三定律**:不可能通过有限的步骤使一个物体冷却到绝对温度的零度; **推论**:$\lim_{T\to0}\left(\frac{\partial V}{\partial T}\right)_p=-\lim_{T\to0}\left(\frac{\partial S}{\partial p}\right)=0,\lim_{T\to0}\left(\frac{\partial p}{\partial T}\right)_V=\lim_{T\to0}\left(\frac{\partial S}{\partial V}\right)_T=0$