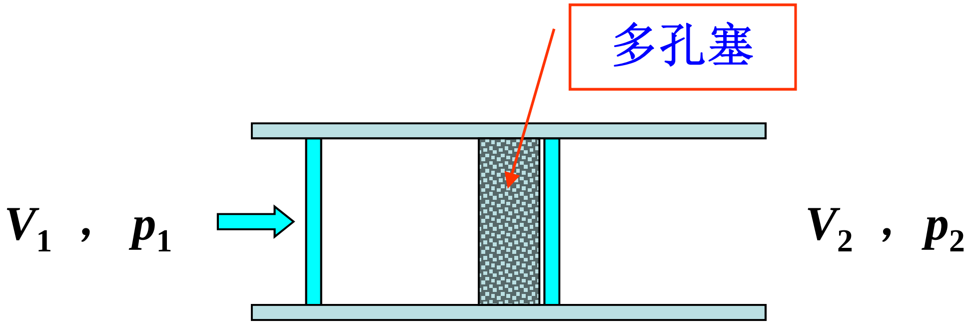
§2.3 气体节流和绝热膨胀

1. 节流

焦—汤效应 气体节流后温度改变。



绝热过程 $Q=0$

外界做功 $W=p_1V_1-p_2V_2$

$$U_2 - U_1 = p_1V_1 - p_2V_2$$

$$H_2 = H_1$$

气体节流后焓不变。

焦一汤系数 $\mu=\left(\frac{\partial T}{\partial p}\right)_H$

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

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

?

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

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

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

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

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

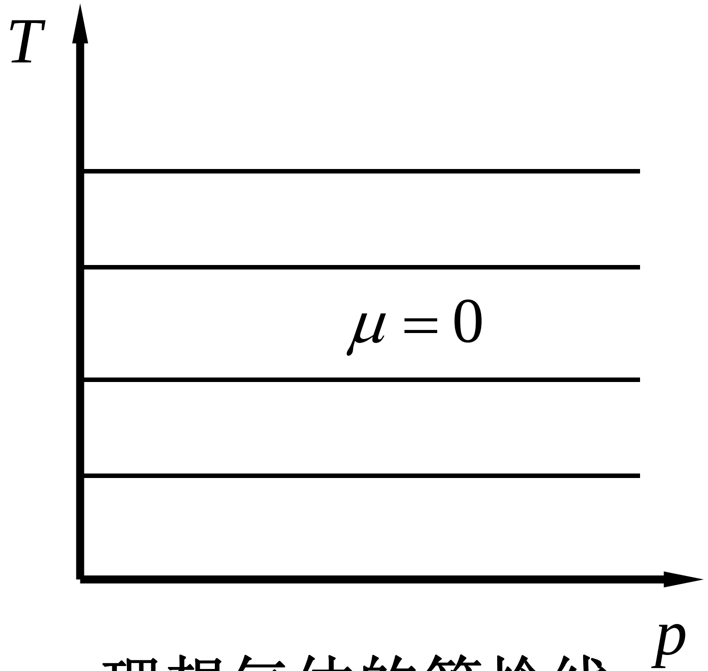
$$H = H(T, p), \quad \mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$$

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

得证

（1）理想气体

$\alpha = \frac{1}{T}$ $\mu = 0$ 节流后温度不变

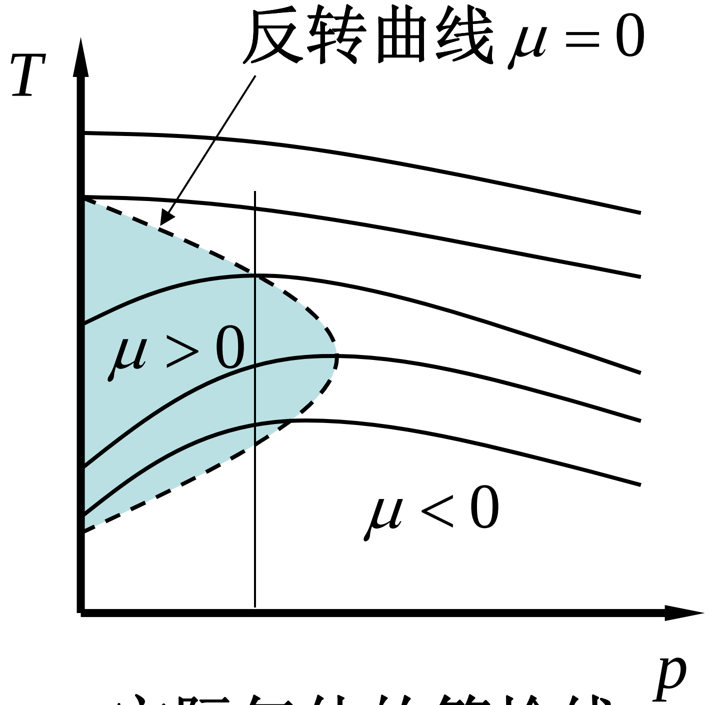


理想气体的等焓线

（2）实际气体

$\alpha > \frac{1}{T}$ $\mu > 0$ 致冷

$\alpha < \frac{1}{T}$ $\mu < 0$ 致热



实际气体的等焓线

温度愈低，制冷效果愈好，但气体必须预冷。

实际气体昂尼斯方程

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

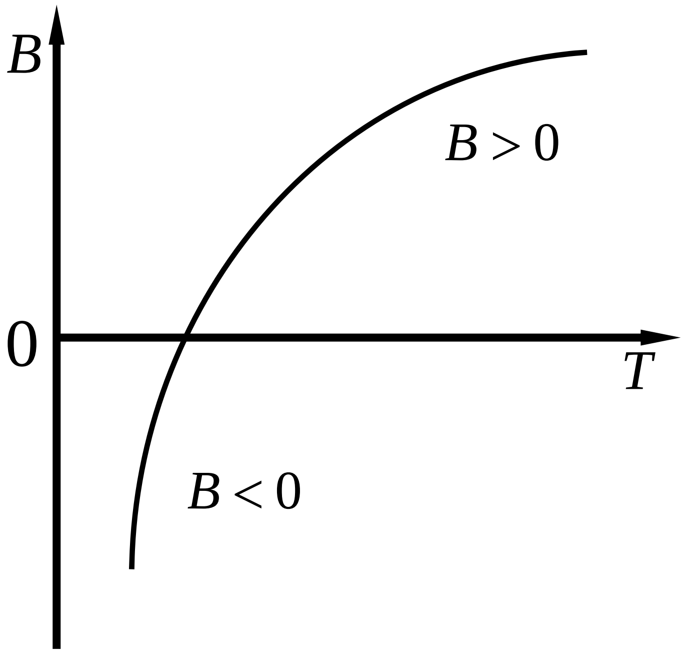
$$p=\frac{nRT}{V}\left[1+\frac{n}{V}B(T)\right] \qquad \because\ \frac{n}{V}B(T)<<1\ \ \therefore \text{可以将}\ \frac{n}{V}=\frac{p}{RT}\ \text{带入}$$

$$p=\frac{nRT}{V}\left(1+\frac{p}{RT}B\right) \qquad V=\frac{nRT}{p}\left(1+\frac{p}{RT}B\right)=n\left(\frac{RT}{p}+B\right)$$

$$\left(\frac{\partial V}{\partial T}\right)_{p}=n\left(\frac{R}{p}+\frac{dB}{dT}\right) \qquad \alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p}=\frac{n}{V}\left(\frac{R}{p}+\frac{dB}{dT}\right)$$

$$\mu=\frac{V}{C_p}(T\alpha-1)=\frac{V}{C_p}\left(\frac{nRT}{pV}+\frac{nTdB}{VdT}-1\right)=\frac{n}{C_p}\left(T\frac{dB}{dT}-B\right)$$

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



$$\frac{dB}{dT} > 0$$

低温下，分子间的吸引大于排斥， $B < 0$， $\mu > 0$ 致冷

高温时斥力的影响，使 $B > 0$, 且$B > T\frac{dB}{dT}$时， $\mu < 0$ 致热

2. 绝热膨胀

$$\mathrm{d}S=\frac{C_p}{T}\mathrm{d}T-\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p \qquad \mathrm{d}T=\frac{T}{C_p}\mathrm{d}S+\frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p$$

$$\left(\frac{\partial T}{\partial p}\right)_S=\frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p=\frac{VT\alpha}{C_p}$$

气体 $\alpha>0$ 致冷

（1）绝热膨胀，$\left(\frac{\partial T}{\partial p}\right)_S$ 恒大于零，也即气体经绝热膨胀后，其温度总是下降的，无所谓的转变温度。

（2）在相同的压强降落下，气体在准静态绝热膨胀中的温度降落大于节流过程中的温度降落。

致冷效果随温度降低而降低，但不需预冷。

§2.4 基本热力学函数的确定

不同的自变量，函数有不同的具体表示式

1. 以T、V为自变量

物态方程 $p = p(T, V)$

内能和熵 $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$

$$S = S(T, V), \quad \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

$$\mathrm{d}U = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]\mathrm{d}V$$

$$\mathrm{d}U = C_V \mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V \qquad \mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V$$

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

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

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

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

已知C_V和物态方程 $p=(T，V)$，由以上公式可以求得U、S

2. 以***T***、***p***为变量

物态方程 $V=V(T,p)$

内能和熵 $\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$ $\mathrm{d}H=T\mathrm{d}S+V\mathrm{d}p$

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

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

$$\mathrm{d}H=C_p\mathrm{d}T+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p \qquad \mathrm{d}S=\frac{C_p}{T}\mathrm{d}T-\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p$$

$$H=\int\left\{C_p dT+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp\right\}+H_0 \qquad S=\int\left[\frac{C_p}{T}dT-\left(\frac{\partial V}{\partial T}\right)_p dp\right]+S_0$$

$U=H-pV$ 测得物质C_p和物态方程，即可得物质的**U**和**S**。

例1 以*T*、*p*为状态参量，求1 *mol*理想气体的*H*、*S*和*G*

$$H_m = \int \left\{ C_{p,m} dT + \left[V_m - T\left(\frac{\partial V_m}{\partial T}\right)_p \right] dp \right\} + H_{m0}$$

$$pV_m = RT \ \Rightarrow \left(\frac{\partial V_m}{\partial T}\right)_p = \frac{R}{p} \qquad \therefore \ V_m - T\left(\frac{\partial V_m}{\partial T}\right)_p = 0$$

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

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

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

$$G_m = U_m - TS_m + pV_m = H_m - TS_m$$

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

$$= RT\left[\frac{1}{RT}\int \frac{C_{p,m}}{T} dT + \frac{H_{m0}}{RT} - \frac{1}{R}\int \frac{C_{p,m}}{T} dT - \frac{S_{m0}}{R} + \ln p\right]$$

$$\varphi(T) = \frac{1}{RT}\int \frac{C_{p,m}}{T} dT + \frac{H_{m0}}{RT} - \frac{1}{R}\int \frac{C_{p,m}}{T} dT - \frac{S_{m0}}{R}$$

只与T有关

通常将G写成： $G_m = RT\left[\varphi(T) + \ln p\right]$

例2.简单固体的物态方程为

$$V(T,p)=V_0(T_0,0)[1+\alpha(T-T_0)-\kappa_T p]$$

试求其内能和熵。

解：

$$V(T,p)=V_0+\alpha V_0 T-\alpha V_0 T_0-V_0\kappa_T p$$

令 $V_1=V_0-\alpha V_0 T_0$ 常数

$$V=V_1+V_0\left[\alpha T-\kappa_T p\right]$$

$$\alpha T-\kappa_T p=\frac{V-V_1}{V_0} \quad \ldots(1)$$

$$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V=T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T+\left[T\left(\frac{\partial S}{\partial V}\right)_T-p\right]\mathrm{d}V$$

$$\mathrm{d}U = C_V \mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p \right] \mathrm{d}V$$

由(1)式 $\alpha - \kappa_T \left(\frac{\partial p}{\partial T}\right)_V = 0$ $\quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$

$$U = \int C_v dT + \int \left[\frac{\alpha T}{\kappa_T} - p \right] dV + U_0$$

$$= \int C_v dT + \int \frac{1}{\kappa_T} (\alpha T - \kappa_T p) dV + U_0$$

$$= \int C_v dT + \int \frac{1}{\kappa_T} \frac{V - V_1}{V_0} dV + U_0$$

$$= \int C_v dT + \frac{(V - V_1)^2}{2\kappa_T V_0} + U_0$$

$$S = S(T, V)$$

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

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

$$= \frac{C_V}{T} dT + \frac{\alpha}{\kappa_T} dV$$

$$S = \int \frac{C_V}{T} dT + \frac{\alpha}{\kappa_T} V + S_0$$

例3.求1 mol的范氏气体的内能和熵。

解：　由物态方程 $\left(p+\frac{a}{v^2}\right)(v-b)=RT$

$$T\left(\frac{\partial p}{\partial T}\right)_V - p = T\frac{R}{v-b} - \left[\frac{RT}{v-b}-\frac{a}{v^2}\right] = \frac{a}{v^2}$$

内能：$u=\int\left\{c_v dT+\frac{a}{v^2}dv\right\}+u_0=\int c_v dT-\frac{a}{v}+u_0$

熵：$s=\int\left[\frac{c_v}{T}dT+\left(\frac{\partial p}{\partial T}\right)_v dv\right]+s_0$

$$=\int\frac{c_v}{T}dT+\int\frac{R}{v-b}dv+s_0$$（注意：c_v与v无关）

最后得：$s=\int\frac{c_v}{T}dT+R\ln(v-b)+s_0$

作业：P73

2.5题，2.8题， 2.9题，

2.10题