§ 2-2 麦氏关系的简单推广及其应用

讨论对象：任意简单系统

求解思路：采用不同的“自变量与状态函数组合”，

找出“实验可测量C_V，C_p，

及物态方程”与状态函数的关系，

从而，由实验可测量求状态函数。

一、T、V为变量U随V变化关系

$$U=U(T,V)$$

选T,V为独立变量，S的全微分为

$$dU=TdS-pdV$$

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

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

得

$$dU=\underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}\,dT+\underbrace{\left[T\left(\frac{\partial S}{\partial V}\right)_T-p\right]}\,dV$$

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

两式比较,即有

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

及

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

- 例： 对理想气体 $pV = RT$

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

得 $$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V} - p = \frac{TR - pV}{V} = 0$$

对理想气体，内能只是温度的函数。

焦耳定律

2、T、p为独立变数，焓的运算关系

$$dH = TdS + Vdp$$

T,p为自变量时全微分为: $$dH = \underline{\left(\frac{\partial H}{\partial T}\right)_p} dT + \underline{\left(\frac{\partial H}{\partial p}\right)_T} dp$$

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

可得 $$dH = \underline{T\left(\frac{\partial S}{\partial T}\right)_p} dT + \underline{\left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]} dp$$

两式比较,即有 $C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$

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

3、简单系统的 $C_p - C_V$

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

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

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

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

在利用麦氏关系

$$C_P - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \Longrightarrow C_p - C_v = \frac{VT\alpha^2}{\kappa_T}$$

例 求证：绝热压缩系数 κ_S 与等温压缩系数之比 κ_T 等于定容热容量与定压热容量之比。

证明： $\kappa_s = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_s, \kappa_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$

$$\frac{\kappa_s}{\kappa_T} = \left(\frac{\partial V}{\partial P}\right)_s \Big/ \left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial S}{\partial P}\right)_V \Big/ \left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$$

$$= -\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \Big/ \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V \Big/ \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{C_P}.$$

4、 任意简单系统基本热力学函数的计算式

(1) 以 T， V 为自变量，计算 U， S

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

C_V

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

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

若已知 C_V 及 物态方程，就可计算 U

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

$$\frac{C_V}{T} \qquad \left(\frac{\partial p}{\partial T}\right)_V$$

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

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

(2) 以 T，p 为自变量，计算 H，S

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

$$\boxed{H=\int\left\{C_p\mathrm{d}T+\left[V-T\left(\frac{\partial V}{\partial T}\right)_V\right]\mathrm{d}p\right\}+H_0}$$

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

$$\boxed{S=\int\left[\frac{C_p}{T}\mathrm{d}T-\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p\right]+S_0}$$

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

例题：求范氏气体的内能和熵

解：范氏气体的物态方程 $$(p+\frac{a}{v^2})(v-b)=RT$$

得： $$(\frac{\partial p}{\partial T})_v=\frac{R}{v-b};\quad T(\frac{\partial p}{\partial T})_v-p=\frac{a}{v^2}$$

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

$$u=\int c_v dT-\frac{a}{v}+u_0$$

由： $$S=\int[\frac{C_V}{T}dT+(\frac{\partial p}{\partial T})_V dV]+S_o$$

$$s=\int\frac{c_v}{T}dT+RT\ln(v-b)+s_0$$

单选题 1分

下列关系成立的是

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

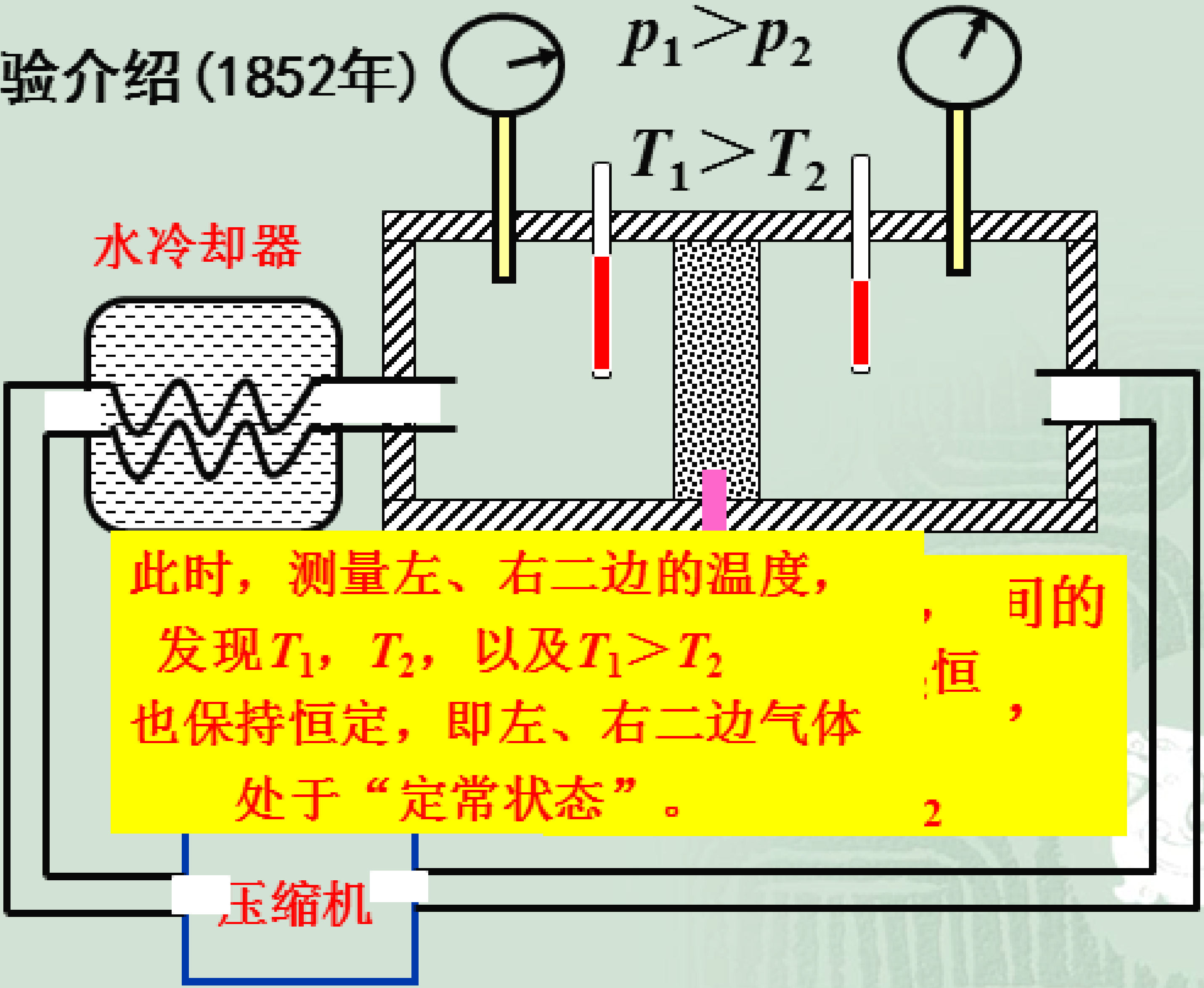
B $U = F - T\left(\frac{\partial F}{\partial T}\right)_V$

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

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

§ 2-3　气体的节流过程和绝热膨胀过程

实验介绍(1852年)



此时，测量左、右二边的温度，
发现T_1，T_2，以及$T_1>T_2$
也保持恒定，即左、右二边气体
处于“定常状态”。

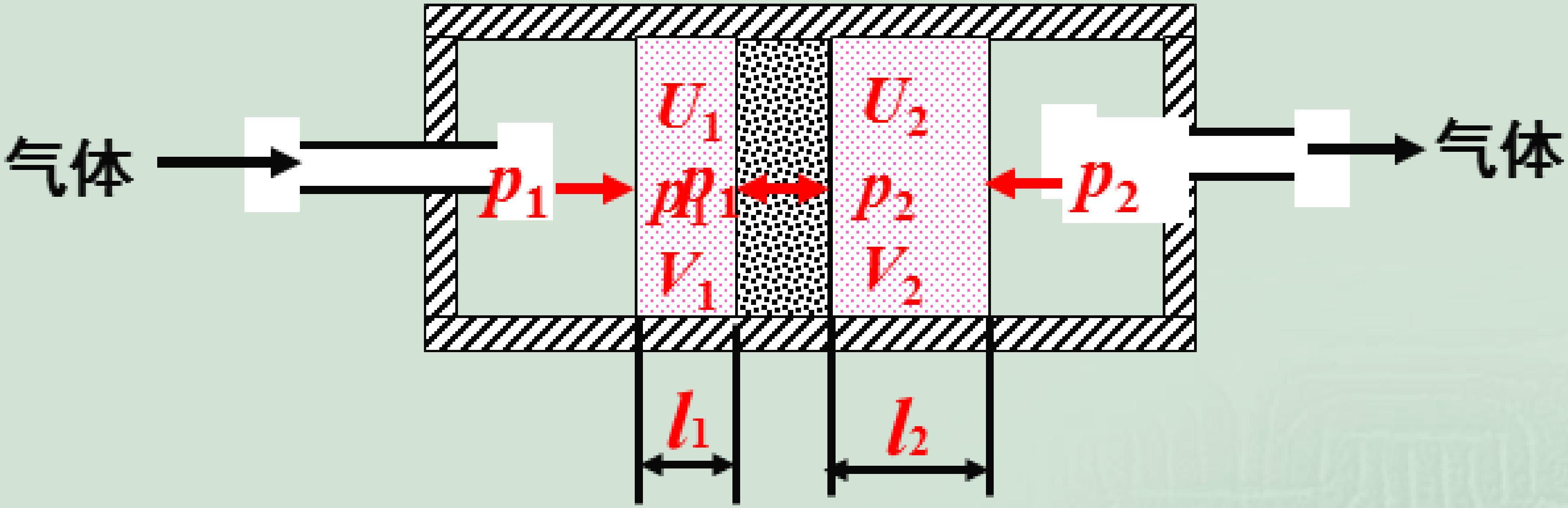
2、实验结论：

①气体经节流过程，其温度降低（焦汤效应）；

②实际气体的内能，不仅与温度有关，
还与其压强、体积有关；

③气体的节流过程为“等焓过程”。

3、结果分析



p_1 将气体 V_1 推出， 做功为 $W_1 = p_1 \times S \times l_1 = p_1V_1$

V_1 进入左边，p_2 做功为 $W_2 = -p_2 \times S \times l_2 = -p_2V_2$

由于气体流动过程为绝热过程，$Q = 0$

同时忽略 V_1，V_2 中气体分子整体运动的动能之差

由第一定律可得：$\Delta U = U_2 - U_1 = W_1 + W_2 = p_1V_1 - p_2V_2$

$$\Delta U = U_2 - U_1 = p_1V_1 - p_2V_2$$

所以有：$U_1 + p_1V_1 = U_2 + p_2V_2$

即：$H_1 = H_2$

节流过程前后焓相等

4、节流过程中温度随压强的变化

定义**焦—汤系数**：焓不变的条件下，气体温度随压强的变化关系。$H=H(T,P)$

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

由于 $H=H(T, p)$

所以有 $\left(\dfrac{\partial T}{\partial p}\right)_H \left(\dfrac{\partial p}{\partial H}\right)_T \left(\dfrac{\partial H}{\partial T}\right)_p = -1$

$$\therefore \quad \mu = -\frac{\left(\dfrac{\partial H}{\partial p}\right)_T}{\left(\dfrac{\partial H}{\partial T}\right)_p} \qquad \boxed{-T\left(\dfrac{\partial V}{\partial T}\right)_p + V} \qquad \boxed{C_p}$$

$$= \frac{V}{C_p}\left[T\alpha - 1\right]$$

焦汤系数的意义分析：

（1）$\mu=\left(\frac{\partial T}{\partial p}\right)_H>0$ 此区域内，温度随压强升高而升高，

温度随压强降低而降低，

故此区域为“降温区”

因为：在此区域内，可采用降低压强的方法来降低温度(气体经节流过程温度降低)

（2）$\mu=\left(\frac{\partial T}{\partial p}\right)_H<0$ 此区域为“升温区”

（3）$\mu=\left(\frac{\partial T}{\partial p}\right)_H=0$

此线为“反转曲线”

为“T，p”关系发生

变化的“曲线”

5、节流降温效应(焦汤效应)的分析

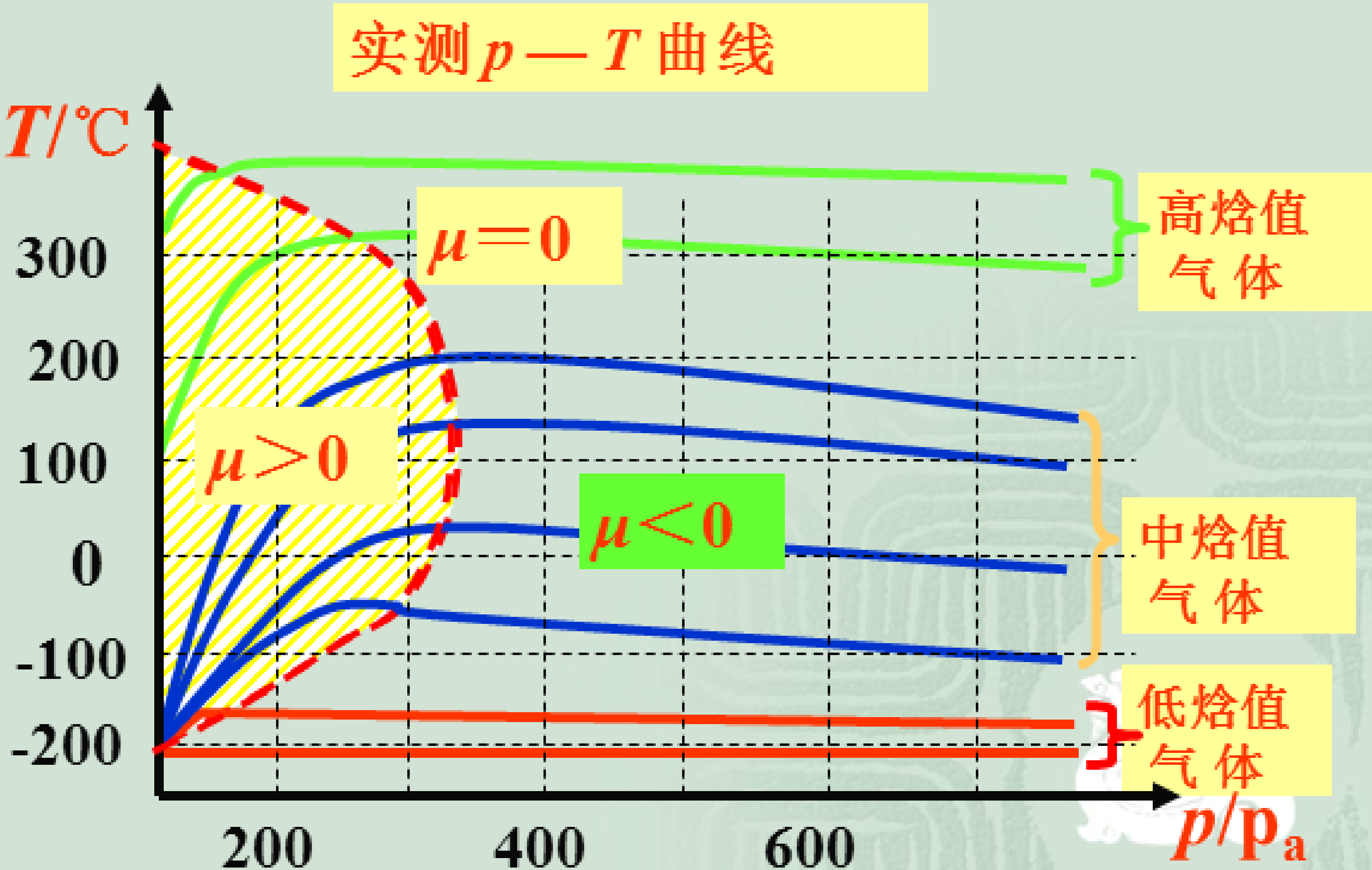
$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}[T\alpha - 1]$$

（1）理想气体

由于 $\alpha = \dfrac{1}{T}$ 所以 $\mu = 0$

故：理想气体经节流过程温度不变化

（2）实际气体　　$a = a(T, p)$


实测p—T曲线
T/℃
300
200
100
0
-100
-200
200
400
600
p/pa
μ=0
μ>0
μ<0
高焓值气体
中焓值气体
低焓值气体

二、绝热膨胀过程中温度随压强的变化

若将实际绝热过程

做为“可逆绝热准静态过程”

则绝热过程为“等熵过程”

那么，温度随压强的变化为：

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

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