# 热力学基本规律

平衡态　$\underbrace{\text{孤立系统}}_{\uparrow\ \text{主要研究}}$(没有物质能量交换)　闭系(没有物质交换,可以有能量)

开系(既有物质交换,又有能量)

Notes: 1° 弛豫时间: 非常短,很快达到平衡 ~$10^{-10}$s (气体典型)

2° 热动平衡:

3° 不考虑涨落: 体系足够大,分子足够多则涨落比较小

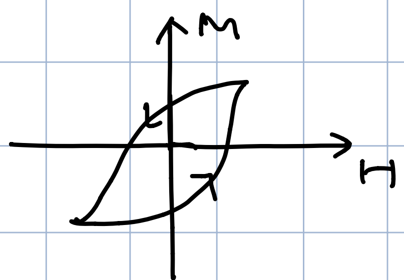
4° 非孤立系统: 处理方法: 所研究的系统+环境=孤立系统

## 状态参量. 状态函数

$\underbrace{\text{几何}: V \quad \text{力学}: p}_{\text{简单系统}}$　化学: $N_i$ ←不同组分　电磁: $\vec{E}, \vec{P}, \vec{H}, \vec{M}$

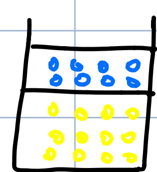
$\vec{P}$: 极化强度　$\vec{M}$: 磁化强度

达到平衡态和达到平衡态前没有关系,与达到平衡的过程无关.




均匀系统: eg 达到平衡后的气体或 $\underbrace{\text{水+水蒸气}}_{\text{2个相}}$　单相系

相: eg. 肉汤, 油里有水, 水里有油



非均匀系统: 复相系

非平衡态

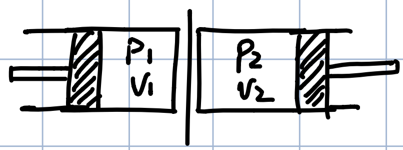
单位: P: $N/m^2$　$P_n=101325Pa \sim 10^5Pa$　mbar　mmHg

$1N=1kg\cdot m/s^2$　标准大气压

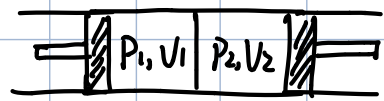
U: J　$1J=1N\cdot m$

# 热平衡定律和温度:

构造一个热平衡系统



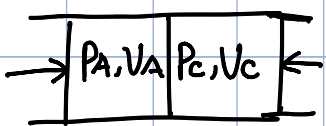

绝热系统




非绝热

$A \rightleftharpoons C$, $B \rightleftharpoons C$ $\Rightarrow$ $A \rightleftharpoons B$ 表示达到平衡

热力学第0定律




$A \rightleftharpoons C$，则存在一个与P,V有关的状态函数f：$f_1(P_A, V_A) = f_2(P_C, V_C)$

$$f_{AC}(P_A, V_A, P_C, V_C) = 0 \Rightarrow P_C = F_{AC}(P_A, V_A, V_C)$$

$B \rightleftharpoons C$ $$f_{BC}(P_B, V_B, P_C, V_C) = 0 \Rightarrow P_C = F_{BC}(P_B, V_B, V_C)$$

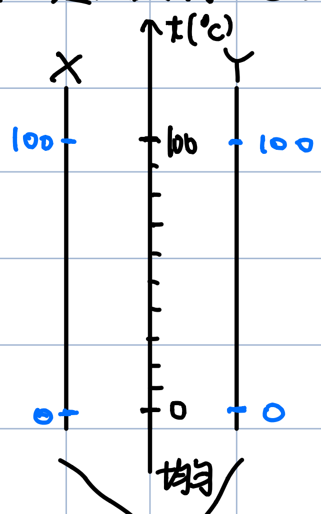
$$\Rightarrow F_{AC}(P_A, V_A, V_C) = F_{BC}(P_B, V_B, V_C) \quad (*)$$

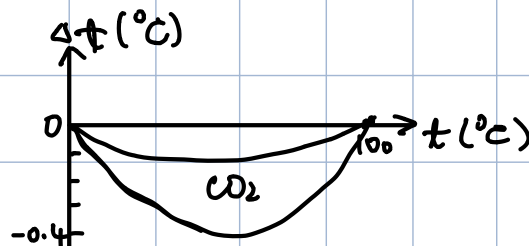
$A \rightleftharpoons B$ $\quad f_{AB}(P_A, V_A, P_B, V_B) = 0$ （与C无关）

说明(*)中不存在与C有关的另

$\Rightarrow g_A(P_A, V_A) = g_B(P_B, V_B)$ 定义为温度 $T_A = T_B$。

如何测量温度？定义温标 ①刻度 ②零标 ③测温物质

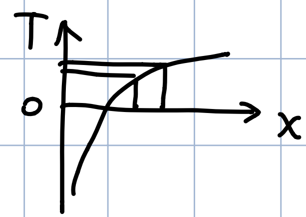


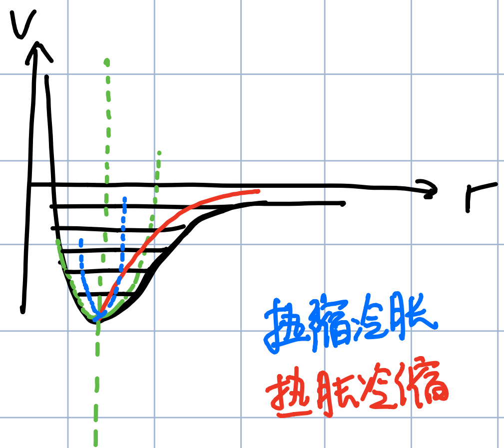

为什么都是往下？

不是线性

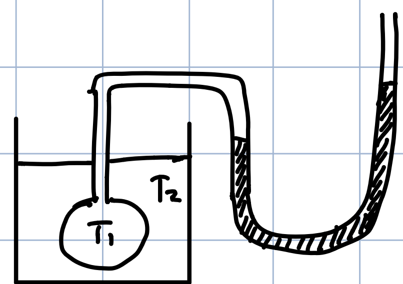
$T=k\ln x$ 适用于易高温. 温度变化小对应于可测量x变化大.



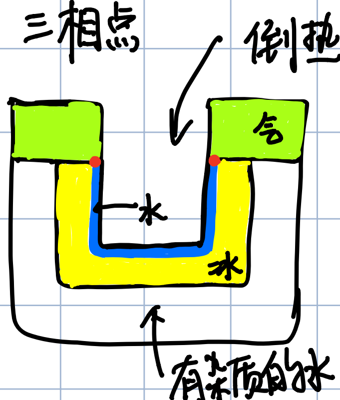

理想气体温标




定容气体温度计 $T \propto P$




三相点




$0.01^\circ C = 273.16K$ $P_{tr}$

$$T_V = \lim_{P \to 0} \frac{P}{P_{tr}} \cdot 273.16K$$

热力学希望有一个温标不依赖于测温物质 —— 热力学温标(恰巧与理想气体温标数值相同)

用到了焦耳定律？

物态方程：理想气体：$PV=nRT$　　$f(P,V,T)=0$

不能由热力学推导，有一部分可以从统计力学推导.

三个系数：体胀系数　$V=V_0+\alpha\Delta T$　$\Delta V=\alpha\Delta T$ ⇒ P,V,T循环

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

$\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P=-1$

$(-V\kappa_T)(P\beta)\left(\frac{1}{\alpha V}\right)=-1$

$\alpha=\kappa_T\beta P$

可以用来测β

压力系数　$\beta=\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$

等温压缩系数　$\kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

为了使结果是正的

Homework: 1.1, 1.2

$PV/T=C$　　$PV=\underset{nR}{\underline{\quad\quad}}T$　what's the coefficient?

$R=8.3145\,J/T\cdot mol$

理想气体：①质点，没有体积.

②没有相互作用.

范德瓦尔斯方程

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$　1mol的情况　考虑与器壁的碰撞

单位物质的量的体积

$n=1$ 时　$v=22.4L=22.4\times10^{-3}m^3/mol$　$P_n=10^5Pa$

以大气压为单位　$(1+20\times10^3a)(v-b)=8.31\times300\times10^{-5}$

$a\sim10^{-5}\sim10^{-6}$

$b\sim10^{-5}$

## 昂尼斯方程

$$p=\frac{nRT}{V-nb}-\frac{an^2}{V^2}\approx\frac{nRT}{V}\left(1+\frac{nb}{V}\right)-\frac{nRT}{V}\left(\frac{an}{TV}\right)$$

$$=\frac{nRT}{V}\left(1+\frac{nb}{V}-\frac{an}{TV}\right)$$

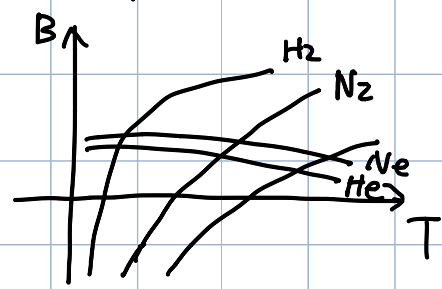
数密度

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

零阶项：理想气体方程

一阶项：范德瓦尔斯方程

维里系数

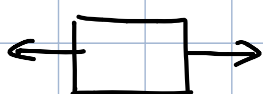



## 简单液体和固体的状态方程

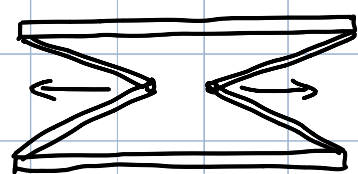
$$V=V(p,T)$$

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

$\alpha \sim 10^{-4}/K$ $\kappa_T \sim 10^{-10}/Pa$

泊松比  理论上允许材料拉长时变粗

拉胀材料（没做出来）



顺磁性固体

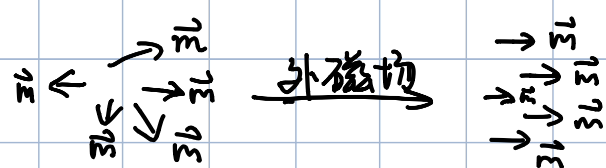
磁化强度 $M=\frac{\Sigma m}{V}$

$$\vec{B}=\mu(\vec{H}+\vec{M})$$

$(\vec{D}=\varepsilon_0\vec{E}+\vec{P}$

$\vec{M}=\chi\vec{H}$ 状态方程 $=\frac{c}{T}\vec{H}$ $\boxed{\text{Curie}}$ 居里定律

$\vec{P}=\varepsilon_0\chi E$ 状态方程$)$




后来发现 $\vec{M}=\frac{C}{T-\theta}\vec{H}$

$T>\theta$ 顺磁

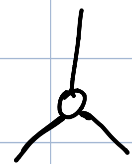
$T<\theta$ 抗磁

所有物质都有抗磁性（楞次定律） 顺磁的磁矩可以转，超过了抗磁性

广延量　$m, V, n$　　$\frac{\text{广延量}}{\text{广延量}}=$强度量

强度量　$T, P, \vec{H}, \vec{E}, \vec{P}$
极化强度

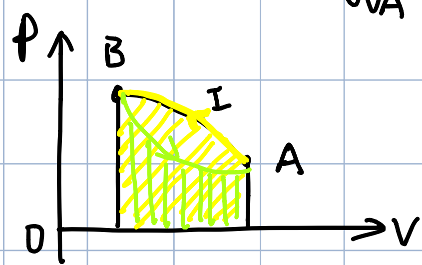
热力学极限　$N\to\infty$，$V\to\infty$，$\frac{N}{V}$有限
粒子足够多　体积足够大




所以高分子一根链（$N\sim10^4$）
也可以做统计.

功　准静态过程　$đW=-pdV$

$V_A\to V_B$　$W=-\int_{V_A}^{V_B}pdV$　对体系做功为正

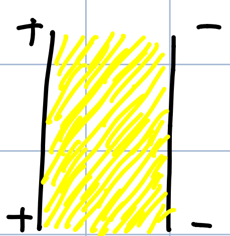



逆时针　外界对体系做正功
顺时针　外界对体系做负功
卡诺循环　外界对体系做负功

非准静态过程　① 等容过程　$W=0$
只能考虑2种过程 ② 等压过程　$W=-p\Delta V$

1° 液体表面膜　$đW=\sigma dA$（$\sigma$：表面张力系数）　拉肥皂膜时要算2个表面

2° 电介质




$đW=Udq$

$đW=Vd(\frac{1}{2}\varepsilon_0E^2)+VEdP$　$(\vec{D}=\varepsilon_0\vec{E}+\vec{P})$

$=V\vec{E}\cdot d\vec{D}$　　$\varepsilon_0=8.85\times10^{-12}F\cdot m^{-1}$

3° 磁介质　$\vec{B}=\mu_0(\vec{H}+\vec{M})$　$\mu_0=4\pi\times10^{-7}H\cdot m^{-1}$　$F=\frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r^2}$

定义的　亨利　测出来的

$đW=V\vec{H}\cdot d\vec{B}$

一般形式下 $đW = Y_i dy_i$　$đW = -pdV$

广义力　广义坐标

热力学第一定律　做功　传热　　能量守恒定律

Joule 1840s-1860s 做的实验

→ 绝热过程中 $U_B - U_A = W_S$

从A点出发，不是所有的B点都能通过绝热过程达到.

如果不是绝热过程 $U_B - U_A - W_S = Q$

$$\Rightarrow U_B - U_A = W_S + Q$$

$$\Rightarrow dU = đW + đQ$$ (Carathéod, 1909)

热容 $C = \lim_{\Delta \to 0} \frac{\Delta Q}{\Delta T}$　广延量　J/K

$c = \frac{C}{m}$　$C_m = \frac{C}{n}$　$C = nC_m$

质量热容　摩尔热容

Homework 1.5 1.6

等容过程　$W = 0 \Rightarrow \Delta U = \Delta Q + W = \Delta Q$　$C_V = \lim_{\Delta T \to 0} \left(\frac{\Delta Q}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$

$\Rightarrow U = U(T, V)$　$C_V(T, V)$

等压过程　$p$ 恒定 $\Rightarrow W = -p\Delta V \Rightarrow \Delta Q = \Delta U - W = \Delta U + p\Delta V$

$$C_p = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = \lim_{\Delta T \to 0} \frac{\Delta U + p\Delta V}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

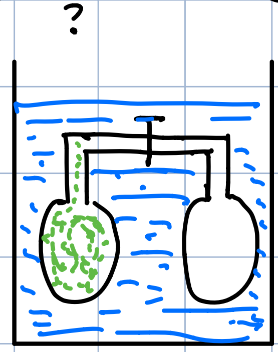
$$= \left(\frac{\partial (U + pV)}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \quad C_p(T, p)$$

焓的物理意义 $H = U + PV$　等压下，焓变 $\Delta H = \Delta U + p\Delta V = \Delta Q$

所以焓的物理意义就是等压下的吸放热

理想气体 $PV = nRT$　$U = U(T, V)$　$U$ 是 $V$ 的函数吗?

焦耳在1845研究了这个问题



$V\to 2V$.

$U$变了吗？(水的温度是否升高)

$(W=0,\ \Delta U=\Delta Q)$

其实$U$与$V$有关，只是实验测不准(因为用的非理想气体)

结论：水的温度不变 $\Rightarrow$ $U$不变 $\Rightarrow U=U(T)$

若$U=U(T,V)$ 则可以构造函数 $f(U,T,V)=0$

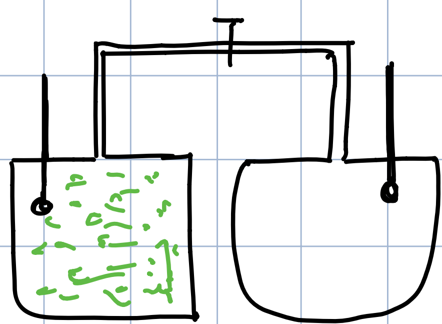
$$\left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_U\underline{\left(\frac{\partial V}{\partial U}\right)_T}=-1 \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T=-\left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_U$$

$$=-C_V\left(\frac{\partial T}{\partial V}\right)_U$$

$\leftarrow$ 焦耳系数 测出来为0

$\Rightarrow U=U(T)$ 焦耳定律

盖·吕萨克 1807



节流实验 1852 焦耳和汤姆逊(开尔文) $W\neq 0$ 等焓过程

$U=U(T,V)$

$$\left.\begin{array}{ll}\text{玻意耳定律} & PV=C(T)\\ \text{阿伏加德罗定律} & V\propto n\\ \text{焦耳定律} & U=U(T)\end{array}\right\}\Rightarrow \text{理想气体}$$

$U$与$V$无关

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=\frac{dU}{dT}\Rightarrow dU=C_V dT\Rightarrow U=\int_{T_0}^{T}C_V dT'+U_0 \underset{\text{理想气体}}{=} C_V\Delta T+U_0$$

$$H=U+PV \qquad C_p=\left(\frac{\partial H}{\partial T}\right)_p=\frac{dH}{dT}\Rightarrow H=\int_{T_0}^{T}C_p\, dT'+H_0 \underset{\text{理想气体}}{=} C_p\Delta T+H_0$$

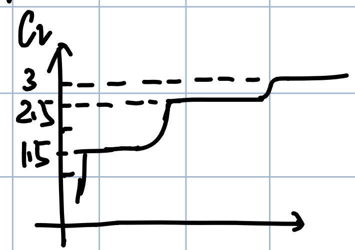
$C_p - C_v = R \quad C_p - C_v = nR \quad \frac{dH}{dT} - \frac{dU}{dT} = nR$

$\frac{C_p}{C_v} = \gamma$ 可以解出 $C_v = \frac{nR}{\gamma - 1} \quad C_p = \gamma \frac{nR}{\gamma - 1}$ $\gamma$是温度的函数吗？

$U = U(T),\ H = H(T) \Rightarrow C_p = C_p(T),\ C_v = C_v(T) \Rightarrow \gamma = \gamma(T)$

但是理想气体 $\gamma$是常数

$U = \frac{3}{2}nRT = \frac{3}{2}Nk_BT \quad c_v = \frac{3}{2}R$ (单原子) $C_v = \frac{5}{2}R$ (双原子,中等温度) $C_v = 3R$ (双原子高温)




理想气体分子有内部自由度.

理想气体绝热过程

$$dU = đQ + dW = dW = -p\,dV$$

$$C_v dT + p\,dV = 0 \xrightarrow{pV=nRT} \left.\begin{aligned} &p\,dV + V\,dp = nR\,dT \\ &C_v dT + p\,dV = 0 \end{aligned}\right\} \Rightarrow p\,dV + V\,dp = -\frac{nR}{C_v} p\,dV$$

$$\Rightarrow p\,dV\left(1 + \frac{nR}{C_v}\right) + V\,dp = 0$$

$$\Rightarrow \gamma p\,dV + V\,dp = 0$$

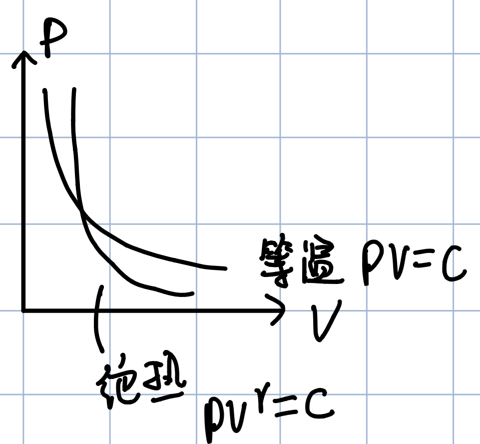
$$\Rightarrow \frac{dp}{p} = -\frac{dV}{V} \cdot \gamma$$

$$\Rightarrow \ln p = -\ln V \cdot \gamma + C$$

$$\Rightarrow pV^\gamma = C$$

$$\xrightarrow{pV=nRT} V^{\gamma-1}T = C$$

$$p^{\gamma-1}T^{-\gamma} = C$$




推导声速用绝热过程

牛顿用等温过程 $v = \left(\frac{dp}{d\rho}\right)^{\frac{1}{2}} = \sqrt{p/\rho}$

Laplace (绝热) 1KHz，热量来不及传递

$$V_s=\sqrt{\left(\frac{dp}{d\rho}\right)_s}=\sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}=\sqrt{\left(\frac{\partial p}{\partial v}\right)_s\left(\frac{\partial v}{\partial \rho}\right)_s}$$

$$=\sqrt{\left(-\frac{p\gamma}{v}\right)(-v^2)}=\sqrt{p\gamma v}=\sqrt{\gamma p/\rho}$$

$\rho=\frac{m}{V}=\frac{1}{v}$

$pv^\gamma=C$

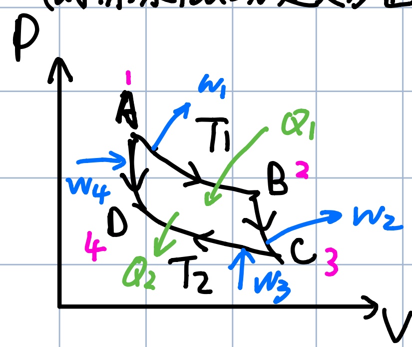
$(V_s)_{Laplace}=\sqrt{\gamma}\,(V_s)_{Newton}$ $\quad \gamma=\frac{C_p}{C_V}=\frac{7}{5}$

$\approx 1.2\,(V_s)_{Newton}$

$0^\circ C$, 1 atm, $V_s=331\,m/s$, $M_m=29\,g/mol \Rightarrow \gamma=1.4$

卡诺循环 (Carnot) 1mol $\quad$ (对体系做功定义为正)

$PV=RT$




$A\to B\to C\to D\to A$

$V_A \quad V_B \quad V_C \quad V_D \quad V_A$

$A\to B \quad đW=-pdV$

$$W_1=-\int_{V_A}^{V_B}\frac{RT_1}{V}dV=-RT_1\ln\frac{V_B}{V_A}$$

$dU=đW+đQ \qquad Q_1=-W_1=+RT_1\ln\frac{V_B}{V_A}$

$B\to C \quad đW=-pdV \quad Q=0$

$$W=-\int_{V_B}^{V_C}\frac{C}{V^\gamma}dV=\frac{C}{\gamma-1}\left(\frac{1}{V_C^{\gamma-1}}-\frac{1}{V_B^{\gamma-1}}\right)=\frac{1}{\gamma-1}(P_CV_C-P_BV_B)$$

$$=\frac{R}{\gamma-1}(T_C-T_B)=C_V(T_C-T_B)=U_C-U_B.$$

Homework. 1.10, 1.11

$C\to D \qquad W_3=RT_2\ln\frac{V_3}{V_4} \qquad Q_2=W_3=RT_2\ln\frac{V_3}{V_4}$

$D\to A \qquad Q=0$

$\Delta U = W + Q \Rightarrow W = Q_1 - Q_2 = RT_1 \ln\frac{V_2}{V_1} - RT_2 \ln\frac{V_3}{V_4}$

$$\left.\begin{array}{ll} B\to C & V_2^{\gamma-1}T_1 = V_3^{\gamma-1}T_2 \\ D\to A & V_1^{\gamma-1}T_1 = V_4^{\gamma-1}T_2 \end{array}\right\} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$\Rightarrow W = R(T_1 - T_2)\ln\frac{V_2}{V_1}$

效率 $\eta = \frac{W}{Q_1} = \frac{R(T_1-T_2)\ln V_2/V_1}{RT_1 \ln V_2/V_1} = 1 - \frac{T_2}{T_1}$ 与具体过程无关，只跟两个热源的温度有关.


斯特令循环 $\eta' = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2}$ 可以大于1

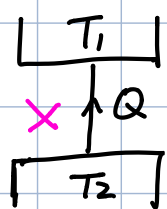
## 热力学第二定律

1842 卡诺

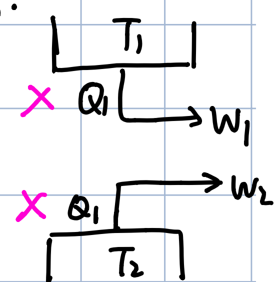
1850 克劳修斯 Clausius

1851 开尔文 Kelvin

Clausius: 不可能把热量从低温物体传递到高温物体而不引起其它变化.

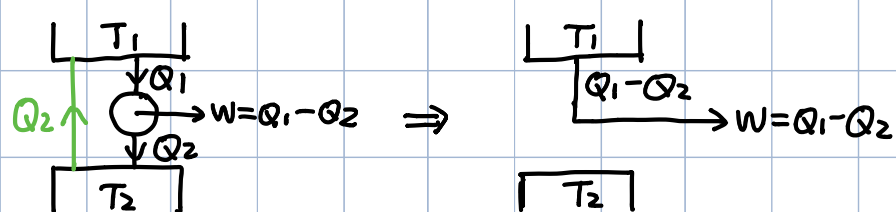



Kelvin: 不可能从单一热源吸收热量，使之完全变成有用功而不引起其它变化.



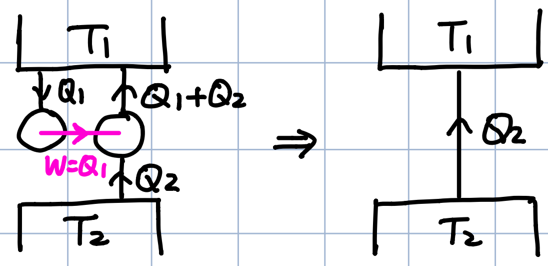

两种说法的等价性

① 如果 Clausius 说法不成立




则开氏说法不成立

② 如果 Kelvin 说法不成立



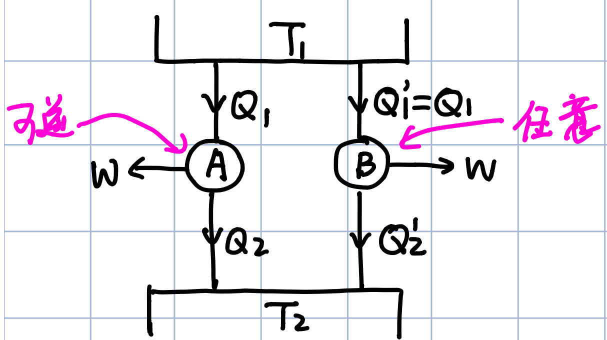

则克氏说法不成立

可逆过程：没有摩擦力的准静态过程.

自然界真实存在的过程都是不可逆过程. 破镜难圆、覆水难收

态函数：熵

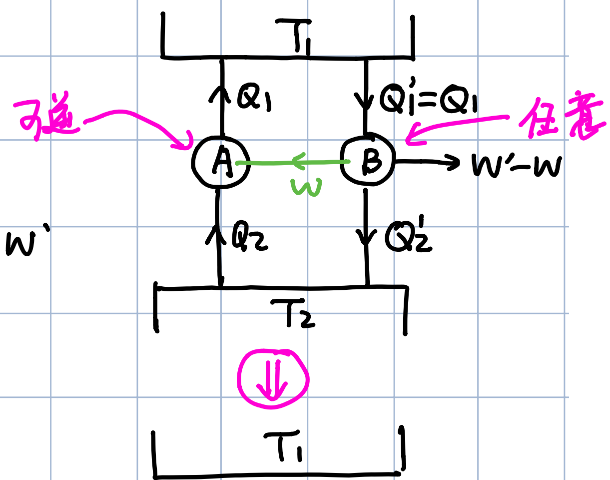
卡诺定理(律)：所有工作于两个热源之间的热机，可逆机的效率最高.



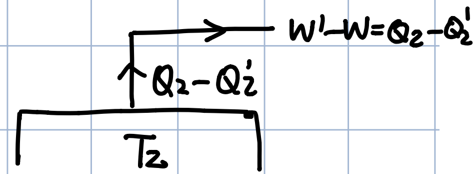

欲证 $\eta_A > \eta_B$

$\boxed{若\ \eta_A < \eta_B}$

$$\left.\begin{aligned}\eta_A &= \frac{W}{Q_1}\\ \eta_B &= \frac{W'}{Q_1'}\end{aligned}\right\} \Rightarrow W < W'$$




Kelvin表述不成立 $\Leftarrow$



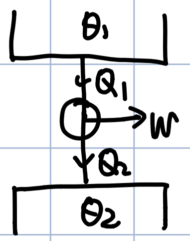

推论：所有工作在两个温度间的可逆机的效率都相等。

$$\left.\begin{aligned}&A可逆: \eta_A \le \eta_B\\ &B可逆: \eta_B \le \eta_A\end{aligned}\right\} \Rightarrow \eta_A = \eta_B$$

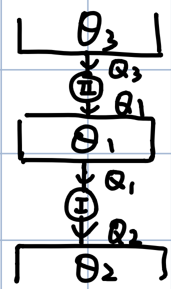
热力学温标($\theta$)

卡诺循环 $\eta = \frac{W}{Q} = \frac{Q_1-Q_2}{Q} = 1 - \frac{Q_2}{Q} = 1 - \frac{T_2}{T}$ 开尔文温标

不依赖于工作物质



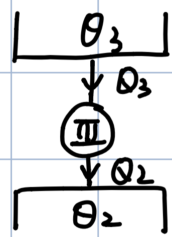

$$\frac{Q_1}{Q_2}=F(\theta_1,\theta_2)$$




$$\frac{Q_3}{Q_1}=F(\theta_3,\theta_1)$$

$$\frac{Q_1}{Q_2}=F(\theta_1,\theta_2)$$

$\Rightarrow$



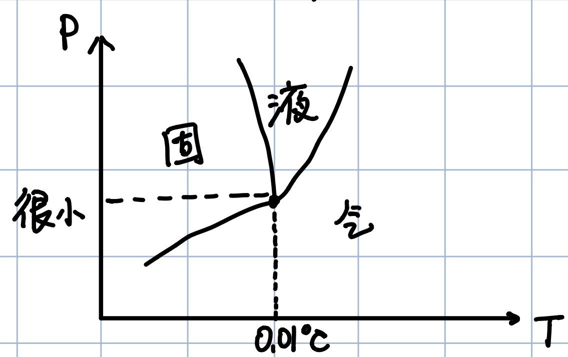

$$\frac{Q_3}{Q_2}=F(\theta_3,\theta_2)$$

$$\Rightarrow \frac{Q_3}{Q_2}=F(\theta_3,\theta_1)F(\theta_1,\theta_2)=F(\theta_3,\theta_2)$$

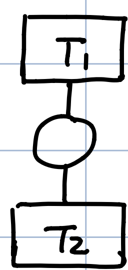
$$\Rightarrow F(\theta_1,\theta_2)=\frac{F(\theta_3,\theta_2)}{F(\theta_3,\theta_1)}=\frac{f(\theta_2)}{f(\theta_1)}=\frac{T_1^*}{T_2^*}$$

1954 水三相点 $T_{tr}=273.16K \to P_{tr}=611Pa=0.006atm$

冰点 $T_0=273.15K \to 1atm=10^5Pa$



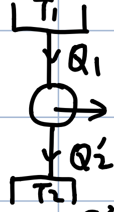

Homework. 1.16. 1.13




$T=\sqrt{T_1T_2}$

Clausius 等式与不等式

$$\eta=1-\frac{Q_2'}{Q_1}\leq 1-\frac{T_2}{T_1}$$




(对外放热为正)

证明思路

直线推论 ⟺ 热力学第二定律 ⟺ 卡诺定理

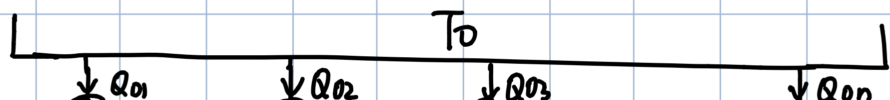
$\Delta S=\frac{Q}{T}$

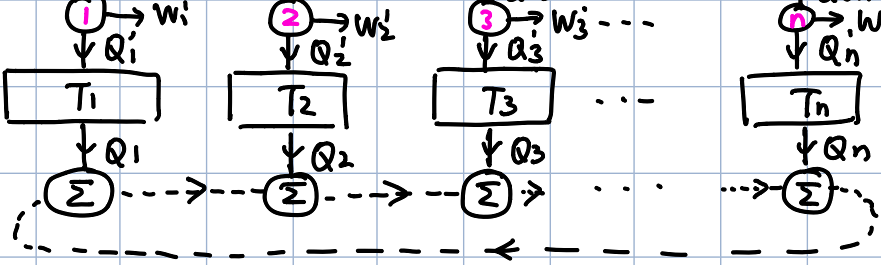
熵增加

$\sum\frac{Q_i}{T_i}\leq 0$

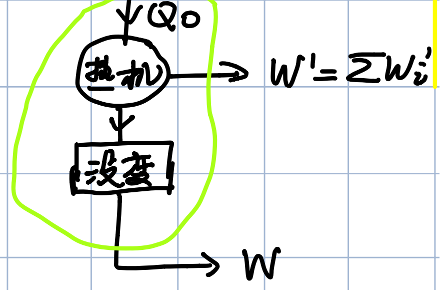
$$\boxed{\frac{Q_2'}{Q_1}\geq\frac{T_2}{T_1}}\Rightarrow\frac{Q_2'}{T_2}\geq\frac{Q_1}{T_1}\Rightarrow\frac{Q_1}{T_1}-\frac{Q_2}{T_2}\leq 0\Rightarrow\frac{Q_1}{T_1}+\frac{Q_2}{T_2}\leq 0$$

欲证 $\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\cdots+\frac{Q_n}{T_n}\leq 0$




⟺




$$\frac{Q_{0i}}{T_0}=\frac{Q_i'}{T_i} \Rightarrow Q_{0i}=\frac{Q_i'}{T_i}T_0$$

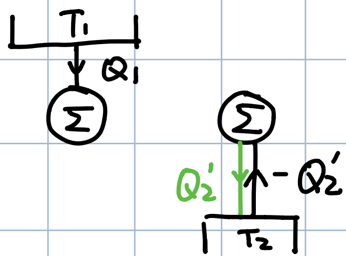
$$Q_0=\sum Q_{0i}=\sum\frac{Q_i'}{T_i}T_0=T_0\sum\frac{Q_i'}{T_i}=T_0\sum\frac{Q_i}{T_i}$$

热力学第二定律

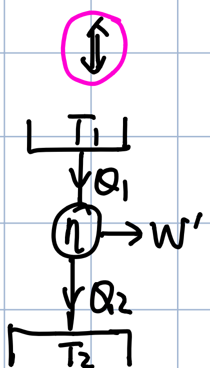
$$Q_0=W'+W\leq 0$$

对外做的功不能是正的

如果只有2个热源




$$\frac{Q_1}{T_1}+\frac{-Q_2'}{T_2}=\frac{Q_1}{T_1}-\frac{Q_2}{T_2}$$




卡诺定理

$$\eta=\frac{W'}{Q_1}=\frac{Q_1-Q_2}{Q_1}=1-\frac{Q_2}{Q_1}\leq 1-\frac{T_2}{T_1}$$

$$\Rightarrow \frac{Q_2}{Q_1}\geq\frac{T_2}{T_1}\Rightarrow\frac{Q_2}{T_2}\geq\frac{Q_1}{T_1}\Rightarrow\frac{Q_1}{T_1}-\frac{Q_2}{T_2}\leq 0.$$

对于可逆热机 → 反转 → $\boxed{Q_i\to -Q_i}$

$$\sum\frac{-Q_i}{T_i}\leq 0\Rightarrow\sum\frac{Q_i}{T_i}\geq 0\Rightarrow\sum\frac{Q_i}{T_i}=0$$

卡诺定理 ⟺ $\left\{\begin{array}{l}\text{开氏表述}\\ \text{克氏表述}\end{array}\right\}$ ⟺ 克劳修斯不等式

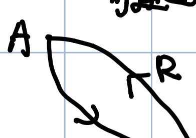
$$\oint\frac{đQ}{T}\leq 0$$

熵 entropy

$\frac{dQ}{T}$ energy transfer

态函数

可逆过程




$$\int_A^B\frac{đQ_{R'}}{T}+\int_B^A\frac{đQ_R}{T}=0$$

$$\Rightarrow \int^B\frac{đQ}{}\ -\int^B\frac{đQ}{}$$

$\Rightarrow \int_A \frac{đQ}{T} - \int_A \frac{đQ}{T} = 0$

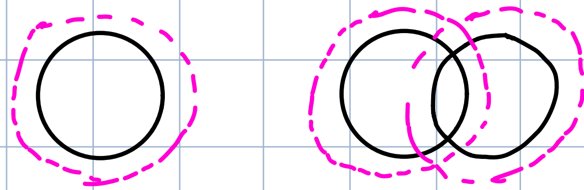
$\Rightarrow$ 态函数

$$S_B - S_A = \int_A^B \frac{đQ}{T}$$

$$dS = \frac{đQ}{T} = \frac{dU - dW}{T} = \frac{dU + pdV}{T} \Rightarrow dU = TdS - pdV$$

广延量 $\propto V$（正比的前提是相互作用可以忽略不计）

$\boxed{\text{depletion}}$



理想气体的熵 $dU = C_V dT \quad pV = nRT$

$$dS = \frac{dU + pdV}{T} = \frac{C_V dT + nRT\frac{dV}{V}}{T} = C_V\frac{dT}{T} + nR\frac{dV}{V}$$

$$\Rightarrow S - S_0 = C_V \ln T + nR\ln V = S(T, V)$$

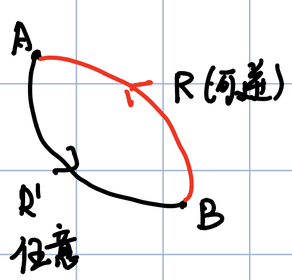
$$dS = \frac{dU + pdV}{T} = \frac{dU + nRdT - Vdp}{T} = (C_V + nR)\frac{dT}{T} - \frac{nR}{p}dp$$

$$\Rightarrow S - S_0 = C_p \ln T - nR\ln p$$

等温过程 $V_A \to V_B \quad \Delta S = nR\ln\frac{V_B}{V_A}$

$V_B > V_A \Rightarrow \Delta S > 0$，吸热，做功

$V_B < V_A \Rightarrow \Delta S < 0$，放热，外界对体系做功



$$\int_A^B \frac{đQ_{R'}}{T} + \int_B^A \frac{đQ_R}{T} \leq 0$$

$$\int_A^B \frac{đQ_{R'}}{T} - \int_A^B \frac{đQ_R}{T} \leq 0$$

$$\int_A^B \frac{đQ_{R'}}{T} \leq \int_A^B \frac{đQ_R}{T}$$

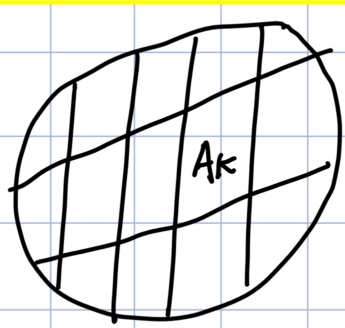
$$\int_A^B \frac{đQ_{R'}}{T} \leq \int dS = \Delta S.$$

$dS \geq \frac{đQ}{T}$ 　绝热系统 $đQ = 0$. $dS \geq 0$ 熵增加原理

$$dU = đQ + đW \leq TdS + đW$$

Homework. 1.17, 1.19.

Examples.

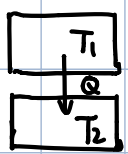



$$A_k \to B_k \xrightarrow{\text{可逆}} A_k$$

$$\left.\begin{aligned} &\int_A^B \frac{đQ}{T} + \sum_{k=1}^{N} \int_{B_k}^{A_k} \frac{đQ}{T} < 0 \\ &\int_{B_k}^{A_k} \frac{đQ}{T} = S_{A_k} - S_{B_k} \end{aligned}\right\} \Rightarrow \sum_{k=1}^{N} (S_{B_k} - S_{A_k}) > \int_A^B \frac{đQ}{T}$$

$$\Rightarrow S_B - S_A > \int_A^B \frac{đQ}{T}$$

$$S_B > S_A$$




$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{-Q}{T_1} + \frac{Q}{T_2} = Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0$$

两杯水混合（假设质量相等）

$$T = \frac{T_1 + T_2}{2} \qquad (T_1, p), (T_2, p) \longrightarrow (T, p)$$

$$dS = \frac{dU - đW}{T} = \frac{dU + pdV}{T} = \frac{dH}{T} = \frac{C_p dT}{T}$$

$$\Delta S_1 = \int_{T_1}^{T} \frac{C_p dT}{T} = C_p \ln \frac{T}{T_1} = C_p \ln \frac{T_1 + T_2}{2T_1} \qquad \Delta S_2 = \int_{T_2}^{T} \frac{C_p dT}{T} = C_p \ln \frac{T}{T_2} = C_p \ln \frac{T_1 + T_2}{2T_2}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = C_p \ln \frac{(T_1 + T_2)^2}{4T_1T_2} = C_p \ln \frac{4T_1T_2 + (T_1 - T_2)^2}{4T_1T_2} > 0$$

理想气体自由膨胀（等温）

$$(T, V_A) \longrightarrow (T, V_B)$$

$$\left.\begin{aligned} S_A &= C_V \ln T + nR \ln V_A + S_0 \\ S_B &= C_V \ln T + nR \ln V_B + S_0 \end{aligned}\right\} \Rightarrow \Delta S = nR \ln \frac{V_B}{V_A} > 0$$

自由能F（亥姆霍兹自由能）

吉布斯函数 G（吉布斯自由能，自由焓）

考虑一个等温过程 $(A, T) \to (B, T)$ $\quad đQ \leq TdS \quad Q \leq T(S_B - S_A)$

$\Rightarrow U_B-U_A-\underset{\sim\sim}{W}\le TS_B-TS_A$

体系对外做功

$\Rightarrow -W\le(U_A-TS_A)-(U_B-TS_B)$

也就是说体系对外做的最大的功

$(-W)_{max}=\underline{F_A}-F_B$

自由能，可以用来做功

束缚能．不能用来做功

$F=U-TS \Rightarrow U=F+\underline{TS}$

$U_A-U_B=(-W)_{max}+Q$

(等温且)没有体积变化的话 $W=0$，$F_A\ge F_B$

自由能只能减小

等温等压下 $dp=0$ $V_A\to V_B$ $W=-p(V_B-V_A)$

$F_A-F_B\ge(-W)_{max}=+pV_B-pV_A$

$(F_A+pV_A)-(F_B+pV_B)\ge0$

$G_A-G_B\ge0$ 吉布斯自由能只能减小 $G=F+pV=U-TS+pV=H-TS$

$H=G+TS$

$G$：自由焓

## 均匀物质的热力学

内能、焓、自由能、吉布斯函数
$$\begin{cases} U \\ F=U-TS \\ G=U-TS+pV=H-TS=F+pV \\ H=U+pV \end{cases}$$

三个基本热力学函数 $U.S.\ (p,V,T)=0$

1° $dU=TdS-pdV=\left(\frac{\partial U}{\partial S}\right)_V dS+\left(\frac{\partial U}{\partial V}\right)_S dV$

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

2° $dH=dU+pdV+Vdp=TdS+Vdp$

$H=H(S,p)$ $\left(\frac{\partial H}{\partial S}\right)_p=T$ $\left(\frac{\partial H}{\partial p}\right)_S=V$ $\left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_p$

3° $dF=dU-TdS-SdT=-pdV-SdT$

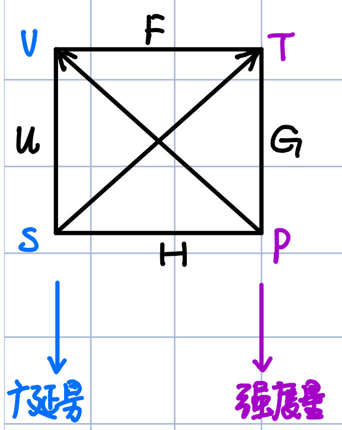
$$F=F(V,T) \qquad \left(\frac{\partial F}{\partial V}\right)_T=-p \quad \left(\frac{\partial F}{\partial T}\right)_V=-S \quad \left(\frac{\partial p}{\partial T}\right)_V=\left(\frac{\partial S}{\partial V}\right)_T$$

4° $dG=dH-TdS-SdT=Vdp-SdT$

$$G=G(p,T) \qquad \left(\frac{\partial G}{\partial p}\right)_T=V \quad \left(\frac{\partial G}{\partial T}\right)_p=-S \quad \left(\frac{\partial V}{\partial T}\right)_p=-\left(\frac{\partial S}{\partial p}\right)_T$$

空间 $(T,V,p,S)$

特性函数 $(U,F,G,H)$




$dU=TdS-pdV=đQ+dW$ $\qquad TdS=đQ \qquad \left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V$

$dF=-SdT-pdV \overset{T}{=} dW$ $\qquad -pdV=dW \qquad -\left(\frac{\partial V}{\partial T}\right)_p=\left(\frac{\partial S}{\partial p}\right)_T$

$dG=-SdT+Vdp=\,?$ $\qquad -SdT=\,? \qquad -\left(\frac{\partial T}{\partial p}\right)_S=-\left(\frac{\partial V}{\partial S}\right)_p$

$dH=TdS+Vdp \overset{p}{=} đQ$ $\qquad Vdp=\,? \qquad \left(\frac{\partial p}{\partial S}\right)_V=-\left(\frac{\partial T}{\partial V}\right)_S$

Homework: 1.23 2.3 2.5

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

$$=C_V dT+\underline{\left(\frac{\partial U}{\partial V}\right)_T} dV$$

$dU=TdS-pdV$

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

$\Rightarrow dU=T\left(\frac{\partial S}{\partial T}\right)_V dT+T\left(\frac{\partial S}{\partial V}\right)_T dV-pdV$

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

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

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

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

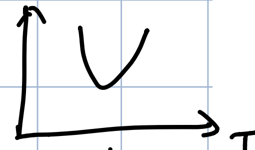
$C_p-C_V=T\left(\frac{\partial S}{\partial T}\right)_p-T\left(\frac{\partial S}{\partial T}\right)_V$

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

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

$\Rightarrow \boxed{C_p-C_V=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p}$ 理想气体 $nR$ $\qquad V$

$$= T\beta p \cdot \alpha V = \frac{V\alpha^2}{\kappa_T} \geq 0 \qquad \alpha = 0 \Leftrightarrow$$




4°C的$H_2O$

Hg 0°C $C_p = 28.0\ J/(K\cdot mol)$ $v = 1.47\times10^{-5}\ m^3/mol$

$\alpha = 181\times10^{-6}\ K^{-1}$ $\kappa_T = 3.94\times10^{-6}\ atm^{-1} = 3.89\times10^{-11}\ Pa^{-1}$

$\Rightarrow C_p - C_v = 3.4\ J/(mol\cdot K)$

Jacobi

$(x,y) \to (u,v)$ $\quad u = u(x,y)$, $v = v(x,y)$

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}$$

性质

1. $\left(\frac{\partial u}{\partial x}\right)_y = \frac{\partial(u,y)}{\partial(x,y)}$

2. $\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}$

3. $\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(r,s)} \cdot \frac{\partial(r,s)}{\partial(x,y)}$

4. $\frac{\partial(u,v)}{\partial(x,y)} \cdot \frac{\partial(x,y)}{\partial(u,v)} = 1$

$$\begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix} = \left(\frac{\partial u}{\partial x}\right)_y.$$