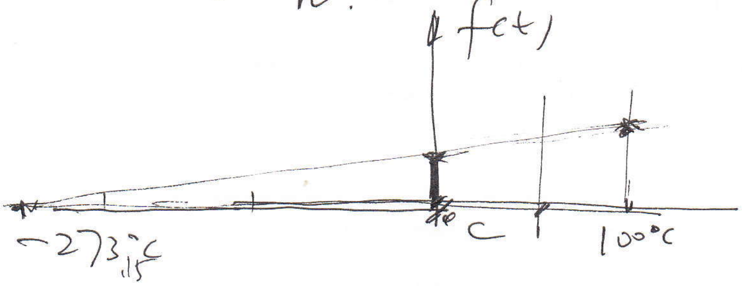
热力学 综述

Any gas $\lim_{P\to 0}(P\bar{V}) = \text{Const.} = \underline{f(t)}$ universal for any gas

$\bar{V} = \frac{V}{n}$,



$$f(T) = \frac{f(T_{tp})}{273.15} T = \lim_{P\to 0}(P\bar{V}), \quad \frac{f(T_{tp})}{273.15} = \bar{R}$$

~~For~~ Ideal gas $\Longleftrightarrow$ P small enough, no molecule interaction

限于P足够小 $P\bar{V} = \bar{R}T$.

$P\frac{V}{n} = \bar{R}T$, $PV = n\bar{R}T$.

$\bar{R}$ universal gas constant $8.314 \frac{kJ}{kmol \cdot K}$

$PVM = nM\bar{R}T$, M, molecular weight

$PV = nM\frac{\bar{R}}{M}T$

$PV = mRT$, $R = \frac{\bar{R}}{M} = \frac{8.314 \frac{kJ}{kmol\cdot K}}{29\ kg/kmol} = 0.287 \frac{kJ}{kg\cdot K}$

$P = \rho RT$, $Pv = RT$.

热力学状态参量, $\underbrace{P, \rho, T, v = \frac{1}{\rho}, u}_{强度}$, $h = u + Pv$, $\underbrace{m}_{广延}$.

知道两个独立的状态参量, 状态就确定下来

$u = u(T, v)$, $du = \frac{\partial u}{\partial T}\Big|_v dT + \frac{\partial u}{\partial v}\Big|_T dv$

Ideal gas. Constant T, compress a little bit, will not affect energy, $\frac{\partial u}{\partial v}\Big|_T = 0$.

$du = \frac{\partial u}{\partial T}\Big|_v dT = C_v dT$.

if $C_v = \text{Const}$. $u_2 - u_1 = C_v(T_2 - T_1)$

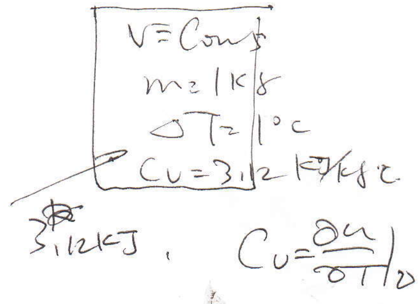
* $h = h(T, P)$

$$dh = \frac{\partial h}{\partial T}\Big|_P dT + \frac{\partial h}{\partial p}\Big|_T dP,$$

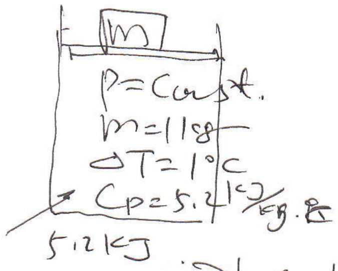
Ideal gas: T same. slight chang in P, will not Change h

$$dh = C_p \, dT,$$

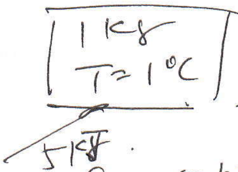
C_p const. $h_2 - h_1 = C_p (T_2 - T_1)$



$C_v = \frac{\partial u}{\partial T}\Big|_v$



$C_p = \partial h / \partial T \big|_P$



Solid $C_p = 5 \text{ KJ/kg°C}$.

* $h = u + Pv$

$$dh = du + d(Pv) = du + R\,dT$$

$$C_p\,dT = C_v\,dT + R\,dT, \quad \Rightarrow C_p = C_v + R.$$

$$\begin{cases} C_p / C_v = \gamma \\ C_p = C_v + R. \end{cases} \Rightarrow C_v = \frac{R}{\gamma - 1}, \quad C_p = R\frac{\gamma}{\gamma - 1}$$

$\gamma = 1.4$ for air

$$C_v = \frac{0.287 \frac{\text{KJ}}{\text{kg}\cdot\text{K}}}{1.4 - 1} \approx 0.717 \text{ KJ/kg K}$$

$$C_p = C_v + R = 0.717 + 0.287 = 1 \text{ KJ/kg}\cdot\text{K}.$$

绝热过程. 从一个状态到另一状态, 无热量传递

$\boxed{1^{st} \text{ law}}$

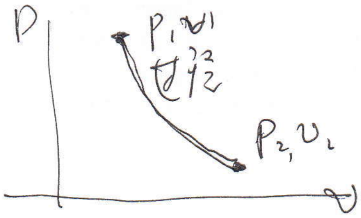
$$du = d\cancel{Q} - P\,dv$$

准平衡过程. 一步步 [illegible] 过程组合

$$du + P\,dv = 0$$

$$C_v\,dT + \frac{RT}{v}\,dv = 0$$

$$\frac{C_v}{R}\int_{T_1}^{T_2} \frac{dT}{T} = -\int_{v_1}^{v_2} \frac{dv}{v} \Rightarrow \frac{C_v}{R}\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{v_1}{v_2}\right)$$



$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\frac{R}{C_v}}, \quad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma - 1}$$

bring in $\frac{Pv}{T} = \text{Const}$. $\quad \frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^{\gamma}$.

等温过程 ~~$0 = dQ - P\,dv$, $dQ = P\,dv =$~~

若等温过程

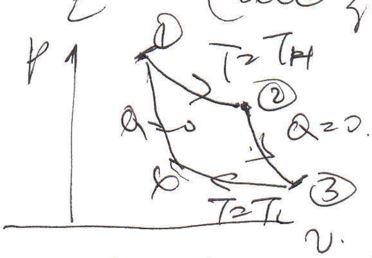
$$du = dq - pdv = 0$$

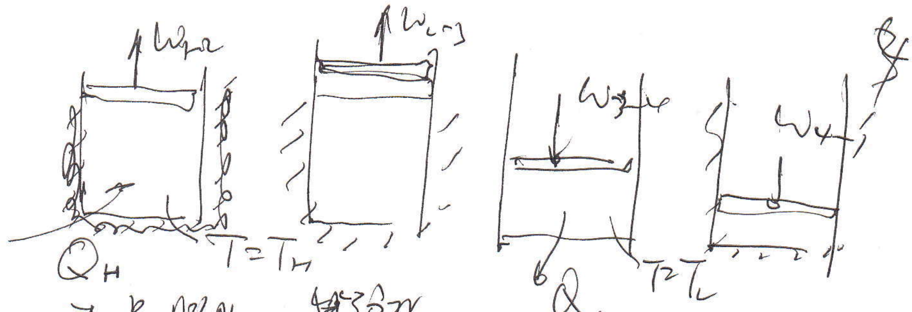
$$dq = pdV = \frac{RT}{v} dv.$$

$$\int dq = RT\int_{v_1}^{v_2} \frac{dv}{v}$$

$$q = RT \ln \frac{V_2}{V_1}$$

~~2nd Carn~~ 循环





等温膨胀. 绝热膨胀

第一类永动机 不可能.

即. 外界温度降与它温相同、外界压强降与内部相同

卡诺循环 Carnot cycle

$$\Delta U = Q_{net} - W_{net} = 0$$

$$Q_H - Q_L = W_{net}.$$

$$\eta = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}\frac{\ln V_4/V_3}{\ln V_2/V_1}$$

因为 2-3, 4-1 绝热 $Tv^{\gamma-1} = C.$

$$\frac{T_L}{T_H} = \left(\frac{v_2}{v_3}\right)^{\gamma-1} = \left(\frac{v_1}{v_4}\right)^{\gamma-1}, \Rightarrow \frac{V_4}{V_3} = \frac{V_1}{V_2}$$

$$\Rightarrow \eta = 1 - \frac{T_L}{T_H}$$

as can.

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \Rightarrow \frac{Q_L}{T_L} = \frac{Q_H}{T_H}$$

可见 $\oint \delta Q \neq 0$ (循环), 但 $\oint \frac{\delta Q}{T} = 0$ for reversible cycles

$\frac{\delta Q}{T}$ 可作为一状态参量，因为其能够[illegible]反映可逆循环特性

$$dS = \frac{dQ}{T}\Big|_{rev} \quad \text{熵}.$$

可逆循环 $\delta Q_{rev} = dU + PdV$

$$\star\ TdS = dU + PdV$$

$$TdS = dU + d(PV) - VdP$$

$$\star\ TdS = dH - VdP$$

$$\Rightarrow \begin{cases} Tds = du + Pdv \\ Tds = dh - vdP \end{cases}$$

$$\begin{cases} ds = \dfrac{du}{T} + \dfrac{P}{T}dv = c_v \dfrac{dT}{T} + \dfrac{R}{v}dv \\ ds = \dfrac{dh}{T} - \dfrac{v}{T}dP = c_p\dfrac{dT}{T} - \dfrac{R}{P}dP \end{cases}$$

S

$$\begin{cases} S(T_2, v_2) - S(T_1, v_1) = \int_{T_1}^{T_2} c_v \dfrac{dT}{T} + R\int_{v_1}^{v_2}\dfrac{dv}{v} \\ \quad = c_v \ln\dfrac{T_2}{T_1} + R\ln\dfrac{v_2}{v_1} \\ S(T_2, P_2) - S(T_1, P_1) = c_p \ln\dfrac{T_2}{T_1} - R\ln\dfrac{P_2}{P_1} \end{cases}$$

Isentropic process $S_2 = S_1$

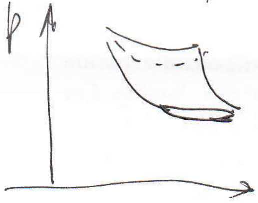
$$0 = c_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{-\frac{R}{c_v}}$$

bring in $\frac{Pv}{T} = \text{const}$.

$$\boxed{\Rightarrow T v^{\gamma-1} = \text{Const.} \quad T P^{(1-\gamma)/\gamma} = \text{Cons}, \; P v^{\gamma} = \text{Const.}}$$

若循环中出现不可逆过程



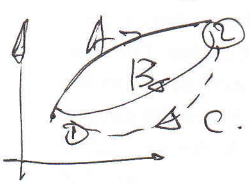
$W_{1-2,不可逆} < W_{1-2,可逆}$，等温膨胀例子.

$W_{net,不} < W_{net,可}$.

$Q_{net\,不} < Q_{,可}$.

$\Rightarrow \oint \frac{\delta Q}{T}\Big|_{不} < 0.$ ，所以有克劳修斯不等式

clausius. $\oint \frac{\delta Q}{T} \le 0.$



A, B 可逆，C 不可逆

$$\cancel{\int_{2\,B}^{1}\frac{\delta Q}{T}\int_1^2}$$

$$\left.\begin{aligned} &\int_{1\,A}^{2}\frac{\delta Q}{T} + \int_{2\,B}^{1}\frac{\delta Q}{T} = 0 \\ &\int_{1\,A}^{2}\frac{\delta Q}{T} + \int_{2\,C}^{1}\frac{\delta Q}{T} \le 0 \end{aligned}\right\}$$

$$\cancel{\int_{1\,A}^{2}\frac{\delta Q}{T} + \int_{2\,C}^{1}\frac{\delta Q}{T} \le 0}$$

$$\cancel{\int_{1\,B}^{2}\frac{\delta Q}{T} + \int_{2\,C}^{1}\frac{\delta Q}{T} = 0}, \quad \cancel{\int_{1\,A}^{2}\frac{\delta Q}{T} + \int_{2\,C}^{1}\frac{\delta Q}{T} \le 0}$$

$$-\int_{2\,B}^{1}\frac{\delta Q}{T} + \int_{2\,C}^{1}\frac{\delta Q}{T} < 0$$

$$\cancel{(S_2 - S_1) \ge \int_{2\,C}^{1}\frac{\delta Q}{T}}, \qquad S_1 - S_2 \ge \int_{2\,C}^{1}\frac{\delta Q}{T}$$

$$\int_{2\,B}^{1}\frac{\delta Q}{T} - \int_{2\,C}^{1}\frac{\delta Q}{T} > 0$$

孤立系统. $\delta Q = 0$, $\qquad S_1 \ge S_2$

逆着②到①的过程

$$S_1 - S_2 > \int_{2\,C}^{1}\frac{\delta Q}{T}$$

绝热系统熵增

孤立系统，同样