Intensive Thermodynamic Variables

$$e \equiv \frac{E}{N} \qquad E\left(\frac{1}{N}S, \frac{1}{N}V, \frac{1}{N}N\right) = e = e(s,v)$$

Extensive properties depend on $\underline{C+2}$ indep. variables
Intensive properties depend on $\underline{C+1}$

$$\left.\frac{\partial e}{\partial s}\right)_v = \frac{\partial}{\partial s}\frac{E(sN, vN, N)}{N} = \frac{1}{N}\frac{\partial(sN)}{\partial s}\frac{\partial E(sN,vN,N)}{\partial sN}$$
$$= T$$

and similarly $\left.\frac{\partial e}{\partial v}\right)_s = -P$

$\therefore$ $\boxed{de = Tds - Pdv}$ differential form, intensive

From $E = TS - PV + \mu N \Rightarrow e = Ts - Pv + \mu \Rightarrow$

$$\mu = e - \left.\frac{\partial e}{\partial s}\right)_v s + \left.\frac{\partial e}{\partial v}\right)_s v = \mu\underbrace{(s,v)}_{C+1 \text{ variables}}$$

Can we express properties in terms of any variables? $\rightarrow$ no, conjugate variable pairs (e.g. s and T, P and v) are not independent.

Example 5.2

At constant V and N, the energy of a perfect crystal near absolute zero is

$E = E_0 + \alpha T^4$ $\qquad E_0, \alpha$ prop. to N, depend on V

Compute $S(T)$ and $S(E)$

$$dE = TdS - PdV + \mu dN = TdS \quad (\text{const. } V \ \& \ N)$$

$$\left.\frac{\partial E}{\partial T}\right)_{V,N} = T \left.\frac{\partial S}{\partial T}\right)_{V,N} = 4\alpha T^3 \Rightarrow \frac{\partial S}{\partial T} = 4\alpha T^2$$

Integrate $\int dS = \int 4\alpha T^2 dT \Rightarrow$

$$S = S_0(V,N) + \frac{4}{3}\alpha T^3$$

To get $S(E)$, solve

$$E = E_0 + \alpha T^4 \Rightarrow T = \left(\frac{E - E_0}{\alpha}\right)^{1/4}$$

$$\therefore \quad S = S_0(V,N) + \frac{4}{3}\alpha\left(\frac{E-E_0}{\alpha}\right)^{3/4} = S_0(V,N) + \frac{4}{3}\alpha^{1/4}(E-E_0)^{3/4}$$

<u>Example 5.3</u>

Find the pressure for this system as $P(T,V,N)$

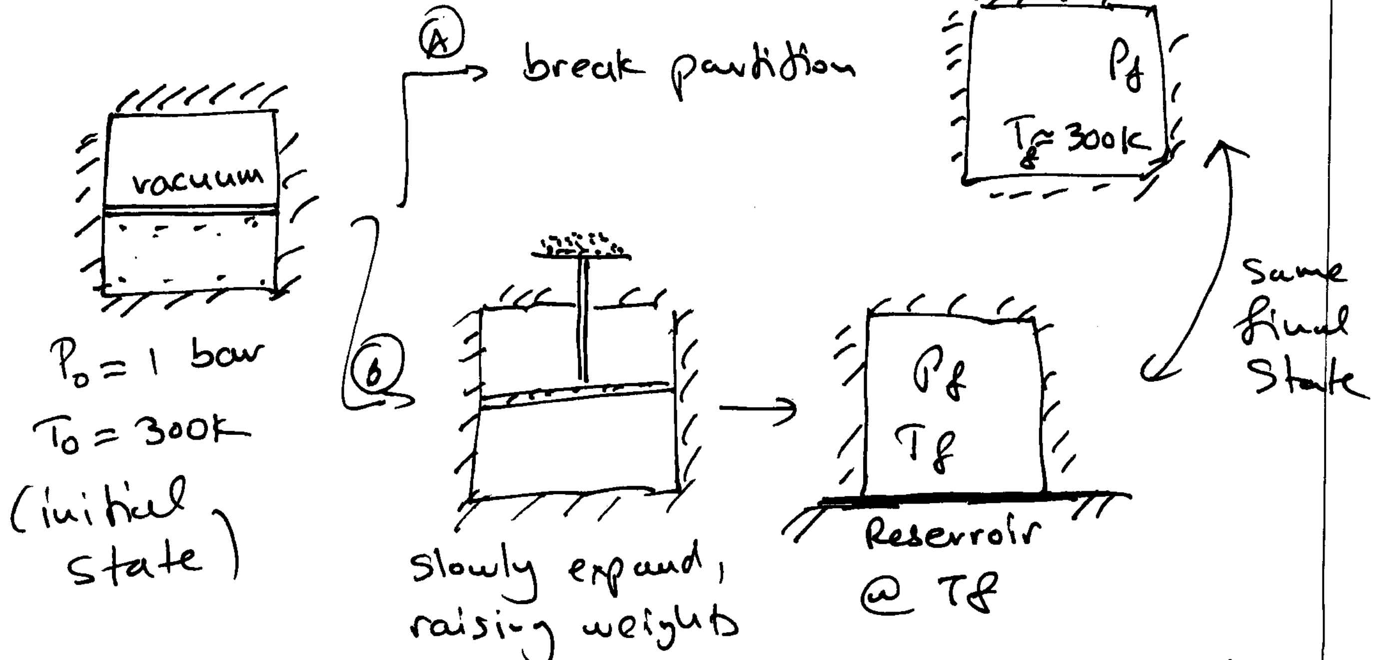
Since $dE = TdS - PdV + \mu dN \Rightarrow \left.\frac{\partial E}{\partial V}\right)_{T,N} = T\left.\frac{\partial S}{\partial V}\right)_{T,N} - P$

$$\Rightarrow P = -\left.\frac{\partial E}{\partial V}\right)_{T,N} + T\left(\frac{\partial S}{\partial V}\right)_{T,N} =$$

$$= -\left[\frac{\partial E_0}{\partial V} + \frac{\partial \alpha}{\partial V}T^4\right]_{T,N} + T\left[\frac{\partial S_0}{\partial V} + \frac{4}{3}T^3\frac{\partial \alpha}{\partial V}\right]_{T,N}$$

$$= -\left.\frac{\partial E_0}{\partial V}\right)_{T,N} + \frac{1}{3}\left.\frac{\partial \alpha}{\partial V}\right)_{T,N} + T\left.\frac{\partial S_0}{\partial V}\right|_{T,N}$$

Not possible to get explicit expression!



$$\underbrace{\Delta E}_{\text{Change in Energy of gas}} = \underbrace{Q}_{\text{heat input}} + \underbrace{W}_{\text{work input}}$$

|| First Law Closed Systems

Q, W, depend on path taken from initial to final state: "inexact" differentials, not state functions

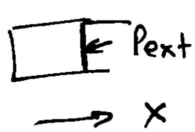
$$\underbrace{dE}= \delta Q + \delta W \quad \text{(differential form)}$$

E is a state function - ΔE only depends on initial + final states

Work

Mechanical work is $\delta W = \vec{F}_{ext} \cdot d\vec{r}$ (done on system)

For 1-d expansion of a gas $\delta W = -P_{ext} A dx$



} note coordinate system $\vec{F}_{ext}$ in opposite direction from dx

If $P_{ext} = P$ (of gas) then $\delta w = -PdV$

E.g., in example on previous page, top case Ⓐ, $P_{ext} = 0 \Rightarrow \delta w = 0$

Other cases $\delta w = \gamma dA$ ← surface

$\delta w = \tau dL$ ← rubber band

$\delta w = \Phi dq$ ← electric charge

From fundamental equation, closed systems

$$dE = TdS - PdV$$

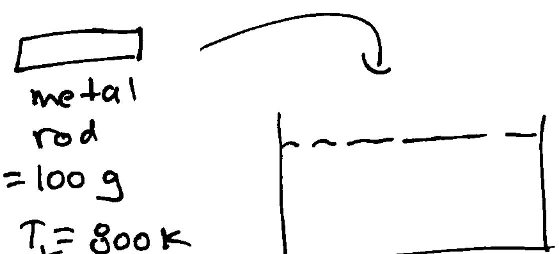
Reversible processes: infinitely slow, no internal or external gradients, no dissipation

→ T, S, P, V well-defined during process (they may be changing slowly)

Since for these processes $\delta w = -PdV \Rightarrow$

$$(\delta Q)_{rev} = TdS \quad \text{or} \quad \boxed{dS = \frac{(\delta Q)_{rev}}{T}}$$

This relationship (which is the basis for the definition of S in classical thermodynamics) can be useful for calculating entropy changes:



metal rod

$m = 100$ g

$T_r = 800$ K

$C_p = 2 \frac{J}{gK}$

water bath

100 kg

$T_b = 300$ K

$\Delta S_{rod} = ?$

$\Delta S_{bath} = ?$

$\Delta S_{universe} = ?$

$T_f = T_b = 300$ K

Clearly irreversible process!

→ devise equivalent reversible processes