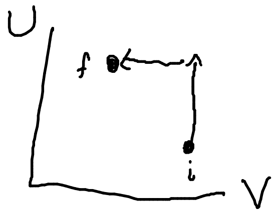
Exam <u>1</u>

February 29th

2 pages of notes + calculator

Ch 1, 2, & a bit of 3

Review Outline will be posted this weekend



Calculate ΔS on this path

$$dS = \underbrace{(dS)_V}_{\text{holding constant}} + (dS)_U$$

$$= \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

$$\boxed{dU = T\,dS - P\,dV}$$

a thermodynamic identity
relationship between changes
true so long as P, T are well-defined (quasistatic)

$$\left(\frac{\partial U}{\partial S}\right)_V \rightarrow dV = 0 \rightarrow dU = T\,dS$$

$$\frac{dU}{dS} = T \longrightarrow \left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

$$0 = T\,dS - P\,dV \rightarrow T\,dS = P\,dV \rightarrow \frac{dS}{dV} = \frac{P}{T}$$

Conjugate variables: T & S $\quad$ P & V

~~only one of each pair~~

$$dU = T\,dS - P\,dV \qquad W = -P\,dV$$

$$dU = Q + W$$

$Q = T\,dS$ even if T is not constant

$\therefore$ $W \neq 0$

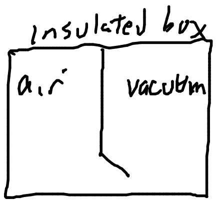
if not quasistatic, more work is necessary

$$W > -P\,dV$$

$$\rightarrow Q < T\,dS$$

$$\rightarrow dS > \frac{Q}{T} \quad \text{more entropy}$$

eg. free expansion



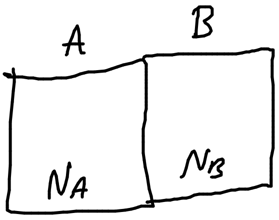
open the door, air rushes into vacuum

$$W = 0 \qquad \text{but} \quad dS \neq \frac{Q}{T}$$

$$Q = 0 \qquad dS > \frac{Q}{T} = 0$$

Diffusive Equilibrium

Let N change



$N_A + N_B = N$

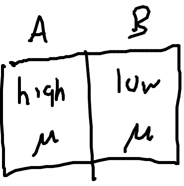
U, V constant

$$\frac{\partial S}{\partial N_A} = \frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B} = 0 \text{ at equilibrium}$$

$\frac{\partial S}{\partial N}$ is same on both sides at equilibrium

Define $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$
chemical potential

$\mu_A = \mu_B$ at equilibrium



U, V const

$$dS_A = -\frac{\mu_A}{T} dN_A$$

$$dS = dS_A + dS_B$$

$$= -\frac{\mu_A}{T} dN_A - \frac{\mu_B}{T} \underbrace{dN_B}_{-dN_A}$$

$$= \frac{1}{T}(-\mu_A + \mu_B) dN_A$$

for spontaneous flow to occur, $dS > 0$

If $\mu_A > \mu_B$ $\quad \frac{1}{T}\underbrace{(-\mu_A + \mu_B)}_{\text{negative}} \underbrace{dN_A}_{\therefore \text{ negative}} > 0$

particles flow from high to low

(just like positive charge and electric potential)

Each type of particle has its own μ.

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$= \frac{1}{T} dU + \frac{P}{T} dV + -\frac{\mu}{T} dN$$

$$\rightarrow \boxed{dU = T\,dS - P\,dV + \underbrace{\mu\, dN}_{\mu_1 dN_1 + \mu_2 dN_2 + \mu_3 dN_3 + \cdots}}$$