

Course 569/669 Lecture Number \_\_\_\_\_ Date 2/27/03Lecturer Dr. Silvia Cavagnero Note Taker Eric FulmerLast Time

$P$  describes tendency to change volume.

$$P = - \left( \frac{\partial U}{\partial V} \right)_{S, N}$$

Thermal definition of pressure.

At equilibrium,  $P_A = P_B$  for a two component system. Usually,  $P = F/A$ . This is good because  $P \cdot dV$  has units of energy.

Chemical Potential

$$\left( \frac{\partial U}{\partial N_j} \right)_{S, V, N_{i \neq j}} = \mu_j$$

At equilibrium,  $\mu$  tends to equalize in an isolated system.

Max Entropy:

$$dS_{\text{TOTAL}} = 0 = \frac{\partial S_A}{\partial N_A} dN_A + \frac{\partial S_B}{\partial N_B} dN_B + \frac{\partial S_A}{\partial U_A} dU_A + \frac{\partial S_B}{\partial U_B} dU_B$$

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Course 565/665 Lecture Number \_\_\_\_\_ Date 2/27/03

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$$\frac{\mu_{A,B}}{T_{A,B}} = \frac{\partial S_{A,B}}{\partial N_{A,B}}$$

Constraint #1:  $U_T = U_A + U_B = \text{constant}$

$$dU_T = dU_A + dU_B \Rightarrow dU_A = -dU_B$$

Constraint #2:  $N_T = N_A + N_B = \text{constant}$

$$dN_T = dN_A + dN_B = 0 \Rightarrow dN_A = -dN_B$$

$$dS_{\text{TOTAL}} = \left( \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dN_A + \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A = 0$$

If at equilibrium,  $T_A = T_B$  (already proven).

$$\frac{\mu_A}{T_A} = \frac{\mu_B}{T_B} \Rightarrow \mu_A = \mu_B$$

At equilibrium, molecules have flown so that chemical potentials are equalized.

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### Reminder

Given a thermodynamic function  $Y$ .  
Go from  $Y_A$  to  $Y_B$ .

$$\Delta Y = Y_{\text{fin}} - Y_{\text{initial}} = Y_A - Y_B$$

If:

- path dependent  $\rightarrow$  State Function.
- path independent  $\rightarrow$  Not a State Function.

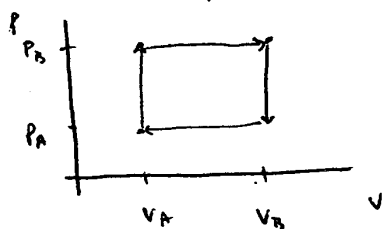
### Common State Functions:

$P, V, T, N, U, S \rightarrow dP, dV, dT, dN, dU, dS$

### Common "Not State Functions"

$w$  (work),  $q$  (heat)  $\rightarrow \delta w, \delta q$

### Thermodynamic cycles.



Initial conditions equal final conditions.

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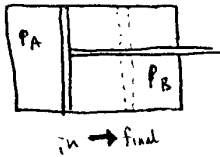
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Quasi-Static Conditions - Go by infinitesimal changes.

Work is maximized.



Quasi-Static Expansion/Compression Work

$$\boxed{\delta w = -P_{\text{ext}} dV}$$

PV work (Very Important).

Sign conventions:

- expansion work (work done by the system),  $\delta w < 0$
- compression work (work done on the system),  $\delta w > 0$

Work at constant Volume

$$\delta w = - \int_{V_{\text{in}}}^{V_{\text{fin}}} P_{\text{ext}} dV = 0$$

There is no PV work done in systems with constant V.

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Work at constant P ( $P_{ext} = \text{constant}$ )

$$W = - \int_{V_1}^{V_2} P_{ext} dV = - P_{ext} \int_{V_1}^{V_2} dV$$

$$W = - P_{ext} (V_2 - V_1)$$

Work at constant T

$$W = - \int_{V_1}^{V_2} P_{ext} dV = \int_{V_1}^{V_2} \frac{NkT}{V} dV$$

$$P_{ext} V = pV = nRT = NkT$$

$$W = - NkT \ln \left( \frac{V_2}{V_1} \right)$$

Ideal Gas Work at constant T.

Principles of Thermodynamics

$$(1) dU = \delta w + \delta q$$

$$(2) dS = \frac{\delta q}{T}$$

Thermodynamic Definition of entropy.