

- agenda
- test-taking tips
  - review lecture
  - problems
  - open questions
- TD is the macroscopic science of systems at equilibrium: <sup>predict their</sup> behaviour.
- Equilibrium: maximize S or minimize U, G... balance of energy (bonds, vibs, etc), entropy (available states), and T (state sampling) matters.
- \* Know how to classify system (every exam!):  
isolated / closed / open / adiabatic

First Law:  $\Delta U = q + w \rightarrow$  overall process calcs. (real processes can't convert  $q \rightarrow w$  100%)

$dU = dq + dw = TdS - PdV + \dots$  heat into or work done on system:  $q, w > 0$

work:  $dw = Fdx$  eq.,  $-PdV$ ;  $(TdS)$ ;  $H(VdB)$ ;  $mdn$

intensive  $\leftarrow$   $\times$  extensive

Gases:  $dw = -PdV$  isobaric =  $-P\Delta V$  iso-T, rev =  $-\int \frac{nRT}{V} dV$   
isochoric = 0

Entropy, 2nd Law:  $\Delta S^{univ} \geq 0$  for spontaneous process.  $\Delta S = \frac{dq_{rev}}{T}$   $C \equiv \frac{dq_{rev}}{dT}$

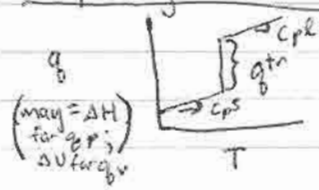
$dS_{(p)} = \int n \frac{C_p}{T} dT$   $\Delta S^{tr} = \frac{\Delta H^{tr}}{T^{tr}}$   $\leftarrow$  main eqs we have used.

$\int n C_p dT = \Delta H = q_p$   
 $\int n C_v dT = \Delta U = q_v$

fyi:  $dS_v = \int n \frac{C_v}{T} dT$   
 $dS_T =$  convert  $dT$  to  $dP$  or  $dV$  from ideal gas law.  $\leftarrow$  TD property calcs.

$dS = \frac{dU}{T} + \frac{PdV}{T} + \dots$  } equil. condition calcs. for equil. properties. using constraints (e.g.,  $dU_A = -dU_B$ )

Graphs: your friends!



- higher slope = higher  $C_p$

$\Delta S$  vs.  $T$  is similar but slope =  $\frac{C_p}{T}$

- Know how to show supercooling/heating: can draw cycles for H, S - because state functions.

- V vs. T gives  $\alpha$  for slope.

- phase fractions: linear transformations.

Misc.

concept: reversible processes (at equil., no dissipation) allow calcs. for real processes at same initial final states (for all state functions).

PDF:  $dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP = TdS + VdP = dH(S, P)$   $\rightarrow$  natural variables.

$U = U(S, V)$ ;  $G = G(T, P)$ ;  $F = F(T, V)$

problems: we went over PS3 #3, #6 on the board.

- I recommended: PS3 #4; Q2003 (like PS3 #6 but check part e.); Q2004 (should be straightforward).