CH160 TEST 2 OUTLINE
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Three Laws of Thermodynamics
1. Energy is always conserved.
2. The entropy of the universe never decreases.
3. The entropy of a crystalline structure at absolute zero has zero entropy.

Energy and Enthalpy
$\Delta H = q_p$ at constant pressure (e.g., coffee-cup calorimetry)
$\Delta U = q_v$ at constant volume (e.g., bomb calorimetry)
Difference between ΔH and ΔU is:
$\Delta H - \Delta U = \Delta(PV) = RT\Delta n$, at constant T, Δn is change in number of moles of gas

Calculating properties for reactions given properties of components
$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$
$\Delta H = \sum BE(\text{reactants}) - \sum BE(\text{products})$ (notice sign reversal here)
$\Delta S = \sum S(\text{products}) - \sum S(\text{reactants})$
$\Delta G = \sum G(\text{products}) - \sum G(\text{reactants})$

For a non-standard temperature, $\Delta H = \Delta C_p \Delta T$

Entropy calculations
$S = k_B \ln W$ (W is number of countable microstates)
$S = k_B \ln 1 = 0$ for crystalline structure with no residual entropy at absolute zero
$S = \frac{q_{rev}}{T}$
$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$ (inequality for irreversible, equality for reversible)
$\Delta_{exp} S = nR \ln \frac{V_2}{V_1}$
$\Delta_{mix} S = -R\left(n_A \ln x_A + n_B \ln x_B\right)$
$\Delta_{vap} S = \frac{\Delta H}{T}$
$\Delta_{heating} S = n\bar{C_p} \ln \frac{T_2}{T_1}$
$\Delta S_{cycle} = 0$

Carnot Heat Engine
$\Delta S = 0$
$q = q_2 + q_1 = nR(T_2 - T_1) \ln \frac{V_2}{V_1}$
$w = -nR(T_2 - T_1) \ln \frac{V_2}{V_1}$
$\text{efficiency} = \frac{|w|}{q_2} = 1 - \frac{T_1}{T_2}$
For a reverse heat engine, $COP = \frac{q_1}{w} = \frac{T_1}{T_2 - T_1}$

For a heat pump, $COP = \frac{q_1}{w} = \frac{T_2}{T_2 - T_1}$

Main energy equations (definitions)
$G = H - TS$ (constant pressure, temperature)
$A = U - TS$ (constant volume, temperature)
$H = U + PV$ (constant pressure)
$U = H - PV$ (constant volume)

Process spontaneous when $\Delta G < 0$ (constant temperature and pressure) or $\Delta A < 0$ (constant temperature and volume); these are equivalent to saying $S_{univ} \leq 0$. If $\Delta G < -10\text{kJ}$, mostly products; if $\Delta G > 10\text{kJ}$, mostly reactants. Process can change spontaneity, namely:

		$\Delta_r H$	
		+	-
$\Delta_r S$	+	At high temperatures	Always
	-	Never	At low temperatures

For processes that do change spontaneity, turning point can be calculated by setting $\Delta G = 0 \Rightarrow T = \frac{\Delta H}{\Delta S}$.
Process endothermic when $\Delta H > 0$

Important total derivatives of main energy equations
$dG = VdP - SdT$
$dA = -PdV - SdT$
$dH = TdS + VdP$
$dU = TdS - PdV$

Basic derivatives of main energy equations
$\left(\frac{\partial G}{\partial P}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_P = -S, \ldots$
e.g., at constant temperature and changing pressure, ΔG is:
$\Delta G = nRT \ln \frac{P_2}{P_1}$ for an ideal gas
$\Delta G = V \Delta P$ for a solid/liquid

Maxwell relations
$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T, \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Derivations of meanings of Helmholtz and Gibbs Free Energies
$dA = dU - TdS = dq_{rev} + dw_{rev} - dq_{rev} = dw_{rev}$ (at constant T)
$dG = dH - TdS - SdT = (dU + PdV + VdP) - TdS - SdT$
$= (dq_{rev} + dw_{rev}) + PdV + VdP - TdS - SdT$
$= TdS - PdV + w_{oth} + PdV + VdP - TdS - SdT = VdP - SdT + w_{oth}$
$= w_{oth}$ at constant (P, T)

Gibbs-Helmholtz equation

Relates temperature dependence of Gibbs energy change to the enthalpy change

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$