Chapter 19: Chemical Thermodynamics
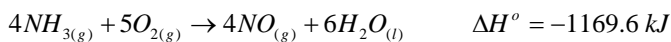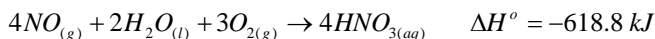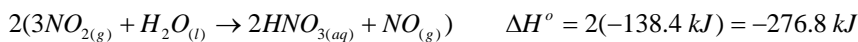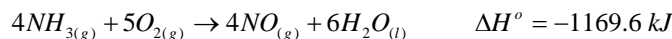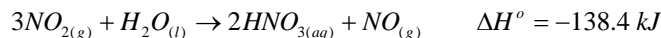
Kahoot!

1. Which process is NOT spontaneous at 25C? melting of an ice cube, sublimation of dry ice, boiling of liquid N_2, freeing of ethyl alcohol
2. Entropy is a measurement of the ___ of a system. randomness, internal energy, temperature, polarity
3. Entropy is a state function, so the change is given by S_{final} ___ $S_{initial}$. +, -, x, /
4. The 2nd law of thermo states that S_{univ} ___ whenever a spontaneous process occurs. increases, decreases, remains unchanged, reaches equilibrium
5. Entropy decreases when ___. a liquid becomes a gas, a solid becomes a liquid, a gas becomes a solid, the number of moles of gas increases
6. Which process does NOT illustrate a decrease in S? $Na_{(s)} + Br_{2(l)} \to 2NaBr_{(s)}$, $CaCO_{3(s)} \to CaO_{(s)} + CO_{2(g)}$, $NH_{3(aq)} + H_2S_{(g)} \to (NH_4)_2S_{(aq)}$, $NH_{3(aq)} + H_2S_{(g)} \to (NH_4)_2S_{(aq)}$,
7. The 3rd law of thermo states that the entropy of a pure, perfect crystal is ___ at 0 K. increasing, decreasing, infinite, zero
8. The pressure, temperature, and units for standard molar entropy are ___. 1 atm; 0C; kJ/mol -K, 1 atm; 298K; J/mol-K, 0 atm; 298K; J/mol-K, 1 atm; 0C; kJ/mol-C
9. Which of the following are true? delta_G = delta_H + T*delta_S, delta_G = delta_H - T*delta_S, delta_G = delta_H x T*delta_S, delta_G = delta_H / T*delta_S
10. If delta_H > 0 and delta_S < 0, the reaction is ___. spontaneous at all T, non-spontaneous at all T, spontaneous at low T, spontaneous at high T
11. If delta_H < 0 and delta_S > 0, the reaction is ___. spontaneous at all T, non-spontaneous at all T, spontaneous at low T, spontaneous at high T
12. At equilibrium, the value of delta_G is ___. +, -, fluctuating, 0

Whiteboard Examples:

Hess's Law Example: Calculate $\Delta H_f^o(HNO_{3(aq)})$ given the following information:

$$\Delta H_f^o(NH_{3(g)}) = -46.1 \, kJ/mol, \, \Delta H_f^o(H_2O_{(l)}) = -285.5 \, kJ/mol$$

$$3NO_{2(g)} + H_2O_{(l)} \to 2HNO_{3(aq)} + NO_{(g)} \quad\quad \Delta H^o = -138.4 \, kJ$$

$$2NO_{(g)} + O_{2(g)} \to NO_{2(g)} \quad\quad \Delta H^o = -114.0 \, kJ$$

$$4NH_{3(g)} + 5O_{2(g)} \to 4NO_{(g)} + 6H_2O_{(l)} \quad\quad \Delta H^o = -1169.6 \, kJ$$

$$2(3NO_{2(g)} + H_2O_{(l)} \to 2HNO_{3(aq)} + NO_{(g)}) \quad\quad \Delta H^o = 2(-138.4 \, kJ) = -276.8 \, kJ$$

$$3(2NO_{(g)} + O_{2(g)} \to 2NO_{2(g)}) \quad\quad \Delta H^o = 3(-114.0 \, kJ) = -342.0 \, kJ$$

$$6\cancel{NO_{2(g)}} + 2H_2O_{(l)} + 4\cancel{6}NO_{(g)} + 3O_{2(g)} \to 4HNO_{3(aq)} + 2\cancel{NO_{(g)}} + 6\cancel{NO_{2(g)}} \quad \Delta H^o = -618.8 \, kJ$$

$$4NO_{(g)} + 2H_2O_{(l)} + 3O_{2(g)} \to 4HNO_{3(aq)} \quad\quad \Delta H^o = -618.8 \, kJ$$

$$4NH_{3(g)} + 5O_{2(g)} \to 4NO_{(g)} + 6H_2O_{(l)} \quad\quad \Delta H^o = -1169.6 \, kJ$$

$$4\cancel{NO_{(g)}} + 2\cancel{H_2O_{(l)}} + 3O_{2(g)} + 4NH_{3(g)} + 5O_{2(g)} \to 4HNO_{3(aq)} + 4\cancel{NO_{(g)}} + 4\cancel{6}H_2O_{(l)} \quad \Delta H^o = -1788.4 \, kJ$$

$$\Delta H_{rxn}^o = 4\Delta H_f^o(HNO_{3(aq)}) + 4\Delta H_f^o(H_2O_{(l)}) - [4\Delta H_f^o(NH_{3(g)}) + 5\Delta H_f^o(O_{2(g)})]$$

$$-1788.4 \, kJ = 4\Delta H_f^o(HNO_{3(aq)}) + 4(-285.5 \, kJ) - 4(-46.1 \, kJ) - 8(0.0 \, kJ)$$

$$\Delta H_f^o(HNO_{3(aq)}) = -207.7 \, kJ$$

Example Entropy of Reaction: Compute the ΔS_{rxn}^o for $C_3H_{8(g)} + 5O_{2(g)} \to 3CO_{2(g)} + 4H_2O_{(g)}$ using the data in Appendix C.

Compound	S^o (J/mol K)
$C_3H_{8(g)}$	269.9
$O_{2(g)}$	205.0
$CO_{2(g)}$	213.6
$H_2O_{(g)}$	188.7

$$\Delta S_{rxn}^o = 3(213.6) + 4(188.7) - [269.9 + 5(205.0)] = 100.7 \, J/K$$

Gibb's Example I: The standard enthalpy and entropy changes for the combustion of methane are -801 kJ and -5 J/K, respectively   Is the reaction spontaneous under standard conditions?

$$\Delta G = -801 \text{ kJ} - 298K * (-5 \text{ J/K} \times 1kJ/1000J) = -803 \text{ kJ}$$

yes it is spontaneous and it is also exergonic

Gibb's Example II: Is the reaction below exothermic or endothermic? Is the reaction spontaneous at all temperature?

Determine the Gibb's free energy from ΔG^o_{rxn} and from $\Delta H - T\Delta S$ at STP

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$
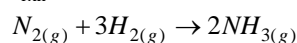
Compound	ΔH^o_f (kJ/mol)	S° (J/mol*K)	ΔG^o_f (kJ/mol)
$N_{2(g)}$	0.0	191.5	0.0
$H_{2(g)}$	0.0	130.6	0.0
$NH_{3(g)}$	-46.1	192.3	-16.5

$$\Delta H^o_{rxn} = 2(-46.1) - [0.0 + 3*0.0] = -92.2kJ$$

therefore it's exothermic

$$\Delta S^o_{rxn} = 2(192.3) - [191.5 + 3(130.6)] = -198.7 J / K$$
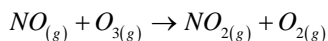
therefore at STP the reaction is spontaneous

$$\Delta G^o_{rxn} = 2(-16.5) - [0.0 + 3(0.0)] = -33kJ$$

Alternatively, we can use $\Delta G = \Delta H - T\Delta S$

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn} = -92.2kJ / mol - 298K(-198.7 J / mol \bullet K) \times \frac{1kJ}{1000J} = -32.99kJ / mol$$

Since both ΔH & $\Delta S < 0$ the reaction will be spontaneous only at low temperatures

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Gibb's Example III: Using the data below calculate ΔG for the reaction at 25°C.

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

	$NO_{(g)}$	$O_{3(g)}$	$NO_{2(g)}$	$O_{2(g)}$
$\Delta G°$ (kJ/mol)	87	163	52	0
Pressure (atm)	1.00 x 10⁻⁶	2.00 x 10⁻⁶	1.00 x 10⁻⁷	1.00 x 10⁻³

$$\Delta G^\circ_{rxn} = \left[(52 + 0) - (87 + 163)\right]\tfrac{kJ}{mol} = -198\tfrac{kJ}{mol}$$

$$Q = \frac{P_{NO_2} P_{O_2}}{P_{NO} P_{O_3}} = \frac{(1.00 \times 10^{-7})(1.00 \times 10^{-3})}{(1.00 \times 10^{-6})(2.00 \times 10^{-6})} = 50.$$

$$\Delta G = \Delta G^\circ + RT \ln Q = -198\tfrac{kJ}{mol} + 8.314\tfrac{J}{mol \bullet K} \times \tfrac{kJ}{1000J} \times 298.15K \ln 50.$$

$$\Delta G = -188\tfrac{kJ}{mol}$$