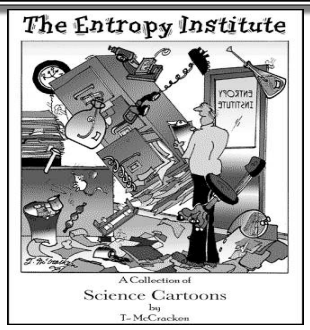
Entropy



Spontaneity

- _____ process – a process that occurs without intervention
  - can be fast or slow

Entropy

- _____(s) – the measure of molecular randomness or disorder
  - Think of entropy as the amount of chaos

Entropy

- Predict which has the highest entropy

1. CO_2 (s) or CO_2 (g)
2. 1 mol of N_2 at 1 atm or 1 mol of N_2 at 0.001 atm

Entropy

- Predict the sign of the entropy change for the following…

1. Sugar is added to water to form a solution

2. Iodine vapor condenses on a cold surface to produce a liquid

2nd Law of Thermodynamics

- 2nd Law of Thermodynamics – In any spontaneous process there is always an increase in entropy of the universe
  - Energy is conserved…entropy is NOT conserved!

3rd Law of Thermodynamics

- The entropy of a perfect crystal at 0K is zero

Free Energy

- _____(G) – a thermodynamic function equal to the enthalpy minus the product of the entropy and the Kelvin temperature
- $\Delta G = \Delta H - T\Delta S$
- A process is only spontaneous in the direction where ΔG is _____

Example

- At what temperatures is the following process spontaneous at 1 atm?
  - $Br_2(l) \rightarrow Br_2(g)$
  - ΔH = 31.0 KJ/mol → 31000 J/mol
  - ΔS = 93.0 J/ K mol

Dependence of H & S on Spontaneity

$\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	Result
-	+	
+	+	
-	-	
+	-	

What is the sign for ΔS?

- $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

- $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Calculating ΔS

- Calculating ΔS is just like calculating ΔH
- Simply use the Appendix…just look at the column for S instead of H
- $\Delta S°$ of any element or diatomic molecule is NOT zero.
- You must look these up!

Example

- Calculate ΔS for the following reaction:
- $2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$

Example

- Calculate ΔS for the following reaction:
- $Al_2O_3(s) + 3H_2(g) \rightarrow 2Al(s) + 3H_2O(g)$

Gibbs Free Energy & Chemical Reactions

- You can calculate ΔG in 3 ways…

1. Like Hess's Law
2. Like $\Delta H°$
3. With the equation $\Delta G = \Delta H - T\Delta S$

Example

- Calculate ΔH, ΔS, & ΔG at 25°C using the following data…
- $2SO_2 + O_2 \rightarrow 2SO_3$

Substance	ΔH (KJ/mol)	ΔS (J/K mol)
SO_2	-297	248
SO_3	-396	257
O_2	0	205

Calculate ΔG

- Using the following data at 25°C
- $C_{diamond} + O_2(g) \rightarrow CO_2(g)$ $\Delta G = -397KJ$
- $C_{graphite} + O_2(g) \rightarrow CO_2(g)$ $\Delta G = -394KJ$
- Calculate ΔG for the reaction:
- $C_{diamond} \rightarrow C_{graphite}$

Calculating ΔG

- Methanol is a high octane fuel used in high performance racing engines. Calculate ΔG for the following reaction
- $2\,CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$
- Given the following free energies of formation:

Substance	ΔG°(KJ/mol)
CH_3OH (g)	-163
O_2 (g)	0
CO_2 (g)	-394
H_2O (g)	-229

ΔG

- Several ways to get ΔG
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G° = nF\varepsilon$
- $\Delta G° = -RTlnK$
- $\Delta G = \Delta G° + RTlnQ$
- R on these is 8.31J/molK

Example

- $N_2 + 3H_2 \rightarrow 2NH_3$
- $\Delta G° = -33.3$ KJ/mol of N_2 consumed at 25 °C. Calculate the value for the equilibrium constant

Example

- Calculate ΔG° at 389 K at equilibrium where $[NH_3] = 2.0M$, $[H_2] = 1.25$ M, & $[N_2] = 3.01$ M
- $N_2 + 3H_2 \rightarrow 2NH_3$

AP Like Questions

- $C(s) + CO_2(g) \leftrightarrow 2CO(g)$
- All 3 of the gases above form an equilibrium mixture by the equation above
- a. Predict the sign of ΔS of the reaction & justify your prediction

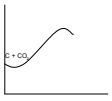
AP Like Questions

- b. In the table below are data that show the % CO in the equilibrium mixture at 2 different temperatures. Predict the sign of ΔH & justify

Temp	%CO
700K	60%
900K	94%

AP Like Questions

- Appropriately complete the energy diagram for the reaction by finishing the graph below. Also clearly label ΔH for the reaction…



AP Like Questions

- d. If the initial amount of C were doubled, what would be the effect of CO? Justify

AP Like Questions

- Will the following be endo or exo?
- Boil H_2O
- Dissolve NH_4Cl (gets colder)
- Dissolving $CaCl_2$ (gets hot)
- Melting ice

AP Like Questions

- NO & CO are air pollutants generated by automobiles. It has been proposed that under suitable conditions these 2 gases could react to form N_2 & CO_2 which are components of unpolluted air.
- a. Write the balanced equation for the reaction described above. Indicate whether C in CO is oxidized or reduced…justify.

AP Like Questions

- b. Write the Kp expression

AP Like Questions

- c. Consider the following thermodynamic data…
- $\Delta G°$ (KJ/mol) NO = +86.55, CO = -137.15, & CO_2 = -394.36
- Calculate the $\Delta G°$ of the reaction
- $2NO + 2CO \rightarrow N_2 + 2CO_2$

AP Like Questions

- d. Given that the ΔH at 298 K is -746 KJ/mol of N_2 formed, calculate ΔS (include units).

AP Like Questions

- e. For the reaction at 298K Kp = $3.33 \times 10^{120.}$ In an urban area the typical pressures of the gases are $P_{NO} = 5.0 \times 10^{-7}$ atm, $P_{CO} = 5.0 \times 10^{-7}$ atm, $P_{N2} = 0.781$ atm, & $P_{CO2} = 3.1 \times 10^{-4}$ atm.
- Calculate the value of ΔG at 298 K with the partial pressures given above.

AP Like Questions

- f. In which direction (Right of left) will the reaction be spontaneous at 298 K with these pressures? Justify