

SPONTANEITY, ENTROPY, AND GIBBS FREE ENERGY

- Many chemical reactions are spontaneous.
- A spontaneous reaction occurs without outside help or intervention.
- Spontaneous reactions can be **FAST** such as combustion of gasoline
- Or **SLOW** such as rusting, or the conversion of diamond to graphite

FIRST LAW OF THERMODYNAMICS

- The total energy of the universe is constant
- Energy can neither be created nor destroyed.
- Energy can be TRANSFORMED.

SECOND LAW OF THERMODYNAMICS

- The ENTROPY of the Universe is increasing.
- Entropy (S)
 - A measure of the DISORDER of a system
 - A thermodynamic function that determines the number of arrangements of the parts of a system.
 - The driving force in spontaneous reactions is an increase in the randomness or disorder.
 - These arrangements are favored by probability.

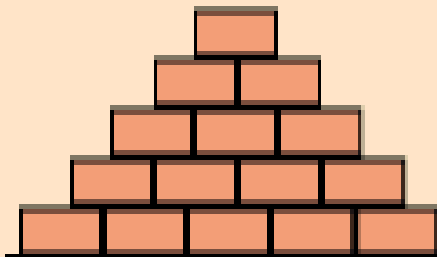
ENTROPY AND SPONTANEITY

- For any given change to be SPONTANEOUS:
 $\Delta S_{\text{universe}}$ must be positive.
- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

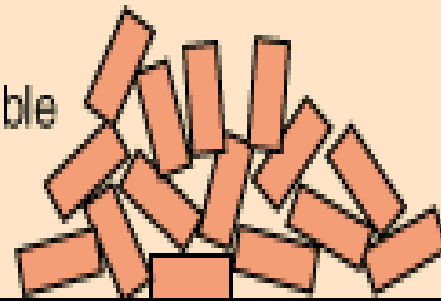
POSITIONAL ENTROPY

- Entropy is favored in part because there are more ways to be disordered than ordered consider.

If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?



Disorder is more probable than order.



GIBBS FREE ENERGY

- **A thermodynamic quantity that is a measure of the useful work that a chemical system can do.**
- **It is related to the system's enthalpy, entropy and temperature.**
- **It predicts spontaneity!!!**

GIBBS APPLIED CONCEPTS

- Gibbs energy is mathematically defined as
- **$\Delta G = H - T\Delta S$** (H in joules, T in kelvins)
- **$\Delta G < 0$ Spontaneous rxn, energy released**
- **$\Delta G = 0$ System at equilibrium**
- **$\Delta G > 0$ Non-spontaneous, energy must be added. Reverse rxn will be spontaneous.**

ENTROPY OF REACTION

- n = number of moles
- Entropy is extensive it depends on the quantity of substance present.

$$\Delta S_{\text{reaction}}^0 = \sum n_p S_{\text{products}}^0 - \sum n_r S_{\text{reactants}}^0$$

Remember to multiply by the number of moles :)

FREE ENERGY CALCULATIONS

- **$\Delta G^\circ = H^\circ - T\Delta S^\circ$**
- **ΔG°** is the change in free energy if the reactants in their standard state are converted to products in their standard state.
- **ΔG°** Cannot be measured directly
- H° and S° are frequently available

Calculations

1) $\Delta G^\circ = H^\circ - T\Delta S^\circ$

reactions are at constant temperature.

2) $\Delta G^\circ_{\text{rxn}} = \sum n_p \Delta G^\circ_p - \sum n_r \Delta G^\circ_r$

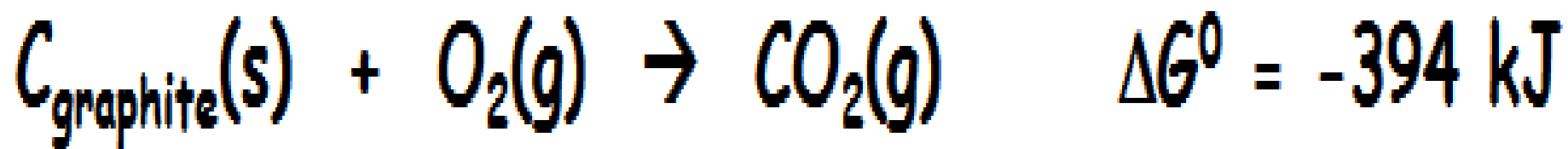
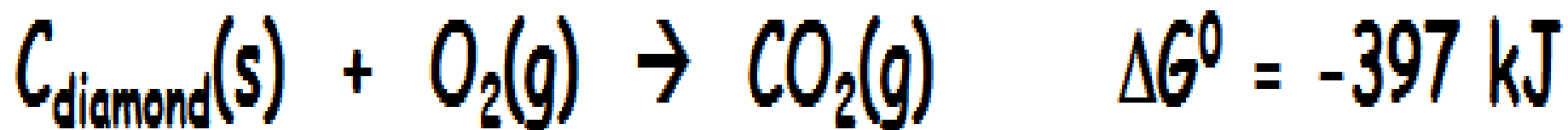
use Hess' Law and sum and cancel until you get the reaction you need.

EXAMPLES

- ◆ Type 1: Calculate ΔG for the phase change:
- ◆ $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ at -10°C , 0°C , and 10°C .
- ◆ Given $\Delta H^\circ = 6.03 \times 10^3 \text{ J/mol}$, $\Delta S^\circ = 22.1 \text{ J/K}\cdot\text{mol}$,

2ND EXAMPLE

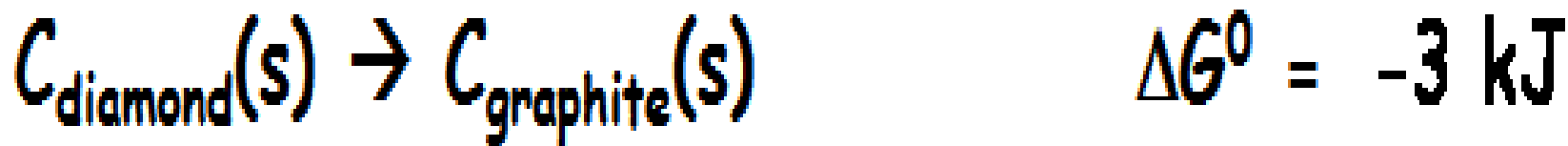
Hess' Law



Calculate ΔG for the conversion of diamond to graphite.

REARRANGE EQUATIONS AND CANCEL

Hess' Law



3RD EXAMPLE

- Calculate the ΔG° for the combustion of methanol. Given:
- $\text{CH}_3\text{OH}_{(g)}$ -163 kJ/mol
- $\text{O}_{2(g)}$ 0 kJ/mol
- $\text{CO}_2_{(g)}$ -394 kJ/mol
- $\text{H}_2\text{O}_{(g)}$ -229 kJ/mol

3RD EXAMPLE

- Balanced Chemical reaction
- $2\text{CH}_3\text{OH} + 3\text{O}_2 \Rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$
- Equation for Gibbs Energy
- $\Delta G^\circ_{\text{rxn}} = \sum n_p \Delta G^\circ_p - \sum n_r \Delta G^\circ_r$
- $(2(-394) + 4(-229)) - (2(-163))$ (elements = 0)
- -1378 kJ

CONNECTING GIBBS TO GAS LAWS!

- S is dependent on Volume
 - Greater volume, greater S
 - Volume and pressure are inversely related so...
- G is dependent on Pressure.
- $\Delta G = G^\circ + \ln(P)$ *This is useful for gases*
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GIBBS RELATED TO K_{eq}

- For gas reactions pressures are directly related to numbers of moles, in turn to concentration.
- Recall that Q (reaction quotient) =
 - $\frac{[\text{products}]}{[\text{reactants}]}$
- ***K_{eq} is called Q when you mix your own concentrations which may be above or below the actual equilibrium values $Q=K$ at equilibrium***

GIBBS AND EQUILIBRIUM

- So $\Delta G = \Delta G^\circ + RT \ln (Q)$
- ΔG is the ΔG of reaction as written
- ΔG° of the sum of the free energies of formation (products – reactants) usually from lists or given in the problem
- R = ideal gas constant in its energy form $8.3145 \text{ J/K}\bullet\text{mol}$
- T is temperature in Kelvins

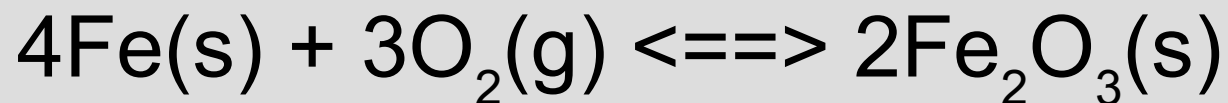
EQUILIBRIUM AND GIBBS

- Equilibrium occurs at the lowest ΔG possible for that system. At equilibrium $\Delta G = 0$ and $Q = K_{eq}$

ΔG^0	K
$\Delta G^0 = 0$	$K = 1$
$\Delta G^0 < 0$	$K > 1$
$\Delta G^0 > 0$	$K < 1$

WHY DO CARS RUST AS THEY AGE?

- Calculate K_{eq} for the reaction at 25°C



- Given ΔH_f° (kJ/mol) S° (J/K•mol)

$\text{Fe}_2\text{O}_3\text{(s)}$	-826	90
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Fe(s)	0	27
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$\text{O}_2\text{(g)}$	0	205
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RUST EXAMPLE

- Since we have no concentration information, we can't write a K_{eq} expression and solve, plus everything but the O_2 is a solid.
Hummmph... what to do?
- Recall that $\Delta G^\circ = RT \ln (K_{eq})$ $K_{eq} = Q$ at
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- We have H's and S' so do the second equation 1st.

(ALCULATING ΔG

- $\Delta H^\circ = \sum H \text{ products} - \sum H \text{ reactants}$
- $\Delta H^\circ = 2(-826) - 0 - 0 = -1652 \text{ kJ or } 1.652 \times 10^6 \text{ J (to match entropy units)}$
- $\Delta S^\circ = \sum S \text{ products} - \sum S \text{ reactants}$
- $2(90) - 3(205) - 4(27) = -543 \text{ J/K}$
- $T = 25 + 273 = 298 \text{ K}$
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- $-1.490 \times 10^6 \text{ J}$ Whoa!!! Your car doesn't have a chance. This reaction is spontaneous

USING ΔG TO FIND K_{eq}

- $\Delta G^\circ = RT \ln (K_{eq})$
- $-1.49 \times 10^6 = 8.3145 \times 298 \times \ln (K_{eq})$
- $\ln(K_{eq}) = 601$
- $K_{eq} = e^{601}$
- And this is a big number!!! So without liberal application of primer, there will be nothing left of your car. Fortunately nothing has been said of the **rate** of reaction. Just that it will go to completion.

ODE TO J. WILLARD GIBBS

- Gibbs Free Energy is probably the most important function in chemistry.
- It tells you whether a given reaction will go or not.
- If it won't go, it tells you how much work you must put into the reaction to get it to go
- If it will go, it tells you how much energy is free to do work outside the system.

COMMENTARY

- Equilibrium requires that processes (reactions) be reversible.
- Entropy is always increasing so if you attempt to reverse a chemical process, you must always supply outside energy to get back to where you started.
- So there is actually no such thing as **perfect** equilibrium.
- All real life reactions are **irreversible**.

THE CYNICS VIEW OF LAWS OF THERMODYNAMICS

- **1st Law of Thermodynamics**
- You can't win, you can only break even
- **2nd Law of Thermodynamics**
- You can't break even. You can't even get out of the game.