

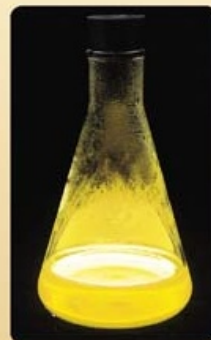
### Reduction of an ion containing vanadium(V) with zinc metal

The yellow color of the  $\text{VO}_2^+$  ion in acid solution.

Zn added. With time the yellow  $\text{VO}_2^+$  ion is reduced to blue  $\text{VO}^{2+}$  ion.

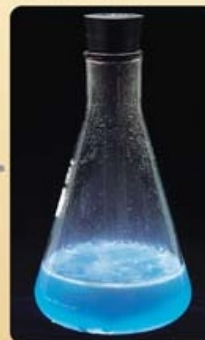
With time the blue  $\text{VO}^{2+}$  ion is further reduced to green  $\text{V}^{3+}$  ion.

Finally, green  $\text{V}^{3+}$  ion is reduced to violet  $\text{V}^{2+}$  ion.



$\text{VO}_2^+$

Add Zn →



$\text{VO}^{2+}$



$\text{V}^{3+}$



$\text{V}^{2+}$

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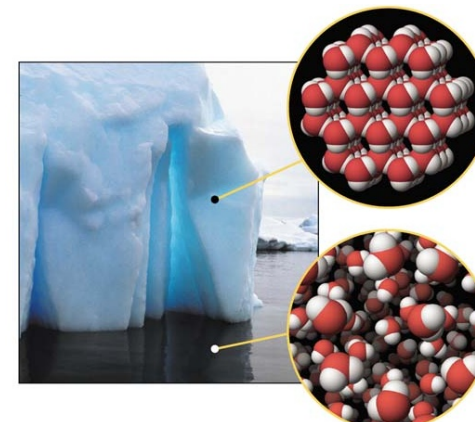
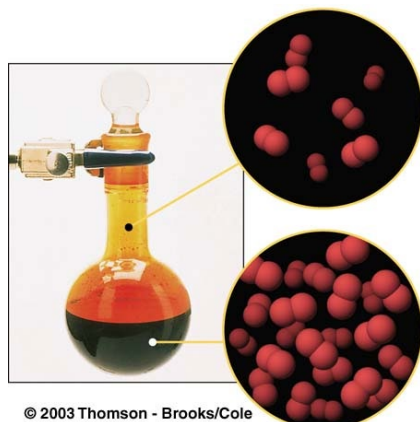
# CHEMISTRY 2000

## Topic #2: Thermochemistry and Electrochemistry – What Makes Reactions Go?

Fall 2020

Dr. Susan Findlay

See Exercises 6.1 to 6.4





# Thermodynamics: The Big Picture

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- When assessing whether or not a reaction can proceed, there are two important things to consider:
  - Thermodynamics tells us whether the products of a reaction are more favourable than the reactants.
  - Kinetics tells us whether there is a reasonable path to get from the reactants to the products.



# Thermodynamics: The Big Picture

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- Before talking about free energy, it is useful to discuss the two main factors that contribute to it:
  - Enthalpy change for a reaction is the heat consumed or released by that reaction (whether a reaction is endothermic or exothermic). Enthalpy is discussed extensively in high school chemistry.
  - Entropy change for a reaction is a measure of whether the system becomes more or less ordered as a result of the reaction.



# A Very Brief Review of Enthalpy (H)

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- Exothermic reactions release heat into the surroundings:  $\Delta H < 0$
- Endothermic reactions absorb heat from the surroundings:  $\Delta H > 0$
- The standard enthalpy change for a reaction can be calculated from standard enthalpies of formation:

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

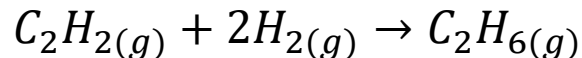
- If a process consists of more than one reaction, the overall enthalpy change for the process is equal to the sum of the enthalpy changes of the individual reactions. This is **Hess' Law**.



# A Very Brief Review of Enthalpy (H)

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- Consider the hydrogenation of ethyne (acetylene gas):



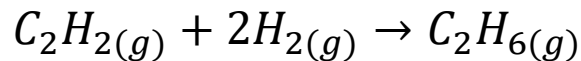
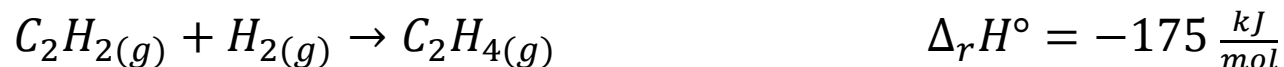
- You could calculate the standard enthalpy change for this reaction using the standard enthalpies of formation of ethyne, ethane and hydrogen:

$$\begin{aligned}\Delta_f H^\circ(C_2H_{2(g)}) &= 227 \frac{\text{kJ}}{\text{mol}} \\ \Delta_f H^\circ(C_2H_{6(g)}) &= -84.667 \frac{\text{kJ}}{\text{mol}} \\ \Delta_f H^\circ(H_{2(g)}) &= 0 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$



# A Very Brief Review of Enthalpy (H)

- Alternatively, you could apply Hess's Law, calculating the standard enthalpy change for this reaction from the standard enthalpy changes for the two steps of this reaction:





# Macroscopic vs. Microscopic States

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- When we analyze a system in the lab, we're looking at its **macroscopic state**:
  - Number of moles of each substance in the system
  - Temperature
  - Total pressure
  - Volume
- These variables are connected by **equations of state**.
  - $PV = nRT$  for ideal gases
  - van der Waals equation for nonideal gases
  - Other equations for solids and liquids



# Macroscopic vs. Microscopic States

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- We can also describe the system's **microscopic state**, or its **microstate**:
  - Position of each particle
  - Momentum of each particle (momentum = mass x velocity)
  - Occupied energy levels for each particle
- This would be a \*lot\* of variables if each particle was considered independently. A system with a mass of  $\sim 1$  mg will contain millions of millions of millions of particles to consider!
- We can take advantage of this very large number of particles in a typical system by taking a statistical approach to thermodynamics. With this many particles, the system as a whole should behave as though it consisted of "average" particles (*even though it doesn't!*) This **statistical approach** allows us to **relate the macroscopic and microscopic states** of a system.





# Entropy, A Statistical Approach

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- The second law of thermodynamics states that “the entropy of the universe increases in any spontaneous process”.  
So, what is entropy?
- Entropy ( $S$ ) is a measure of how many different microscopic states could correspond to the observed macroscopic state:

$$S = k_B \ln \Omega$$

where  $k_B$  is the Boltzmann constant ( $1.380649 \times 10^{-23} \frac{J}{K}$ ) and  $\Omega$  is the total number of microscopic states which would be consistent with a given macroscopic state.

- Systems that are highly ordered (e.g. a perfect crystal at very low temperature) will have very few microscopic states consistent with the observed macroscopic state. On the other hand, systems with less order (e.g. a gas at high temperature) will have many possible microscopic states.



# Entropy, A Statistical Approach (\$25 Example)

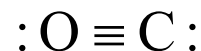
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- Entropy can be considered to be a measure of our ignorance of the microstate of a system. It measures the amount of information needed to reconstruct the microstate.  
e.g. My sister tells me she has \$25 in bills. How many possible microstates (in this case, how many combinations of bills) could correspond to her statement?  
In other words, what is the “entropy of \$25”?



# Entropy, A Statistical Approach (CO Example)

- CO is a polar molecule, but its dipole moment is relatively small. As such, the difference in energy between  
 $:\text{C} \equiv \text{O}:$   $:\text{C} \equiv \text{O}:$  and  $:\text{C} \equiv \text{O}:$   $:\text{O} \equiv \text{C}:$  (or  $:\text{O} \equiv \text{C}:$   $:\text{C} \equiv \text{O}:$ )  
is not large.
- As a result, when CO is frozen, the molecules line up more or less randomly – depending which way they happened to be oriented before freezing. Because, in a crystal, they can't rotate to switch the positions of the C and O atoms, they get “stuck” in this original orientation. They will, however, be lined up (one way or the other). So, each CO molecule has two possible orientations:





# Entropy, A Statistical Approach (CO Example)

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- Thus, the number of possible microscopic states for a sample of solid CO containing  $N$  molecules is:



# Entropy, A Statistical Approach (CO Example)

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- We can therefore calculate the entropy *associated with orientational freedom* in this sample of frozen CO to be:
- Dividing both sides by  $N$  (#molecules) gives us the entropy per molecule *associated with orientational freedom*:
- Multiplying by Avogadro's number ( $N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$ ) gives the theoretical molar entropy ( $S_m$ ) *associated with orientational freedom*:  
  
*Conveniently,  $R = N_A k_B$*
- Experimentally, this contribution to the entropy of solid CO is  $\sim 5 \text{ J/mol}\cdot\text{K}$  – so the orientation of molecules in solid CO is mostly random.



# Entropy, A Statistical Approach

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- Properties of entropy
  - For any given macroscopic state, there is a fixed number of microscopic states that could apply. Thus, the value for the entropy of a given macroscopic state is fixed. As such, entropy is a **state function**. It depends only on the macroscopic state of the system.
  - The change in entropy of a system depends only on the initial and final states – not on the path taken from one to the other. This is true for any state function.
  - If a system has  $\Omega$  possible microstates then doubling the size of the system will double the entropy (by increasing the number of possible microstates to  $\Omega^2$ ). Thus, entropy is an **extensive property**. It depends on sample size.



# Reversibility and Reaction Paths

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- While entropy is a **state function**, heat and work are **path functions**. The amount of heat delivered to a system (or work done on a system) depends on the path taken to carry out the process.
- A special class of paths – **reversible paths** – play a special role in thermodynamics. A reversible process is one during which the system and its surroundings are constantly in equilibrium. Consider two examples of reversible paths:
  - Reversible heat transfer:
  - Reversible expansion of a gas:
- For either of these processes to actually occur, the equilibrium can't be perfect; there must be some small deviation from equilibrium in order for the process to proceed. As long as the deviation is small enough, the concept of a reversible process is a very useful one.



# Entropy, A Thermodynamic Approach

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- Classical thermodynamics allows us to calculate the **change** in entropy for a process:

$$\Delta S = \int \frac{dq_{rev}}{T}$$

where  $q_{rev}$  is the heat for the process along a reversible path and  $T$  is temperature (in K).

- For **isothermal** processes (\_\_\_\_\_), this equation can be simplified to:

$$\Delta S = \frac{q_{rev}}{T}$$

- To calculate the entropy change, we therefore need to know the heat along a reversible path.





# Entropy, A Thermodynamic Approach

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- Consider the entropy change associated with a phase change.  
e.g. At atmospheric pressure, water freezes at 0 °C. The molar heat of fusion (melting) for water at this temperature is 6007 J/mol.
  - (a) Do you expect ice melting to have a positive or negative entropy change?
  - (b) Calculate the entropy change for ice melting at 0 °C.
  - (c) Calculate the entropy change for water freezing at 0 °C.



# The Second Law of Thermodynamics

The entropy of the universe increases in any spontaneous process.

- A “spontaneous” process is one that is thermodynamically favourable according to some path. Depending on the paths available, it may or may not occur.  
e.g. The reaction of hydrogen gas and oxygen gas to make water is “spontaneous”; however, it will not occur without an initial energy input such as a spark.
- It is important to note that it is the entropy **of the universe** that must increase for a spontaneous process. This means that a process with a negative entropy for the system **may** still be favourable **if** it increases the entropy of the surroundings!

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$



# The Second Law of Thermodynamics

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- Intuitively, we can predict that the entropy change for water freezing in a  $-20\text{ }^{\circ}\text{C}$  freezer will be \_\_\_\_\_. Yet, we know that water freezes at this temperature! We must remember to factor in the entropy change for the surroundings (in this case, the freezer) as well as the entropy change for the water:



# The Third Law of Thermodynamics

The entropy of a perfect crystal approaches zero as the temperature approaches absolute zero.

- This law allows us to define an **absolute entropy scale** by defining the entropy of a perfect crystal at 0 K as  $S = 0 \frac{J}{mol \cdot K}$
- Because the entropy of a substance increases with temperature, all pure substances have positive absolute entropies at any non-absolute-zero temperature. (*Solvated species sometimes have negative entropies because the entropy has incorporated "organizing the solvent" effects.*)
- Entropy values for substances in the standard state (1 bar, 25 °C) are commonly tabulated (see Appendix D of Petrucci) and can be used to calculate entropy changes for processes.

$$\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

*\*\*\*Remember to factor in the stoichiometry!\*\*\**



# The Third Law of Thermodynamics

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e.g. Propane ( $C_3H_8$ ) is burned near room temperature so that the water produced is liquid (rather than water vapour). Calculate the entropy change for this reaction.

$$S^\circ(C_3H_{8(g)}) = 270.3 \frac{J}{mol \cdot K}$$

$$S^\circ(O_{2(g)}) = 205.1 \frac{J}{mol \cdot K}$$

$$S^\circ(CO_{2(g)}) = 213.7 \frac{J}{mol \cdot K}$$

$$S^\circ(H_2O_{(l)}) = 69.91 \frac{J}{mol \cdot K}$$



# The Third Law of Thermodynamics

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- Intuitively, we would predict that the burning of propane is spontaneous – even at room temperature – and we would be correct. What is contributing to the negative entropy change?
  
  
  
  
  
  
  
  
  
  
- How can the reaction be spontaneous if it has a negative entropy change?



# The Third Law of Thermodynamics

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- We have to be careful when we use our intuition to predict whether an entropy change will be positive or negative. Consider the reaction in which solid magnesium fluoride is dissolved in water. Calculate the entropy change for this reaction then rationalize the sign of the entropy change.

$$S^\circ(\text{MgF}_{2(s)}) = 57.24 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$S^\circ(\text{Mg}_{(aq)}^{2+}) = -138.1 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$S^\circ(\text{F}_{(aq)}^-) = -13.8 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$



# The Third Law of Thermodynamics

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