

Unit 4 Review 3

RECAP AND ENTROPY

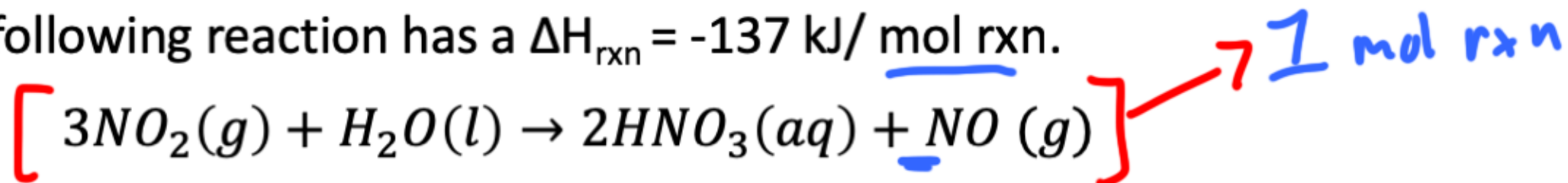
Exam 4 Approaches...

- **Work ALL 92 questions from the bonus worksheets and re-do the homework**
 - WARNING: Do **NOT** treat these like “busy work.” Work the questions slowly and carefully. Your grade on the exam will reflect how much you learned from the process of working these problems, not whether or not you completed them
- **As always, I template out some of the hardest exam-style questions in my reviews**
 - Make sure to visit my slides from throughout the unit and be very confident in the types of questions that I work
- **Extra office hours Q&A!**
 - Friday, 3-5 pm in Bur 112

ECIS
Please do
mine! ;)

Warm Up - ΔH_{rxn} Stoichiometry

As written, the following reaction has a $\Delta H_{\text{rxn}} = -137 \text{ kJ/mol rxn}$.



8 moles of HNO_3 are added to 3 moles of NO gas to run the reverse reaction. What is the ΔH for this process? Answer in kJ.

$$\Delta H_{\text{reverse}} = +137 \text{ kJ/mol rxn}$$

$$8 \text{ moles HNO}_3 \times \frac{1 \text{ mol rxn}}{2 \text{ mol HNO}_3} = 4 \text{ mol rxns}$$

$$3 \text{ moles NO} \times \frac{1 \text{ mol rxn}}{1 \text{ mol NO}} = \boxed{3 \text{ mol rxns}}$$

$$\frac{137 \text{ kJ}}{\text{mol rxn}} \times 3 \text{ mol rxn}$$

$$\boxed{= 411 \text{ kJ}}$$

Today's Equations

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \rightarrow \text{2nd Law}$$

$$S = k \ln \Omega \rightarrow \text{statiscal/microview} \rightarrow \text{conceptual}$$

$$\Delta S = q_{\text{rev}} / T = \frac{J}{K}$$

$$\Delta S = n C_p \ln(T_f / T_i) \rightarrow \Delta T$$

$$\Delta S_{\text{trans}} = \Delta H_{\text{trans}} / T_{\text{trans}} \rightarrow \text{no } \Delta T$$

$$\Delta S_{\text{rxn}}^{\circ} = \sum n S^{\circ} (\text{products}) - \sum n S^{\circ} (\text{reactants}) \rightarrow \text{"Hess' Law equivalent"}$$

Entropy!

ENTROPY IS A MEASURE OF ENERGY DISPERSAL

Big Picture of Thermodynamics

Our universe has finite energy and is constantly expanding. In other words, our universe has a finite capacity to do work and the entropy (energy dispersal) of the universe is always increasing. A chemical reaction is spontaneous when it helps the universe along this path, meaning it has a favorable heat flow ($\Delta H < 0$, exothermic, lowers the energy) and/or a favorable change in entropy ($\Delta S > 0$, positive change in the dispersal of energy).

- A **Spontaneous Reaction** is a reaction that proceeds without the continual input of energy
- A change in a state function is **favorable** when it helps the universe reach a lower energy state
- A favorable change is exothermic ($\Delta H < 0$) or a positive change in entropy ($\Delta S > 0$). A spontaneous reaction can have one favorable term or two, but no spontaneous reaction can have both unfavorable terms.
- A reaction is at **equilibrium** when the rate of the forward reaction is equal to the rate of the reverse reaction, meaning neither reaction is **favored** and no net reaction is observed.
- A **non-spontaneous** reaction can happen, but it requires the continual input of energy

The 2nd Law of Thermodynamics

$$S = \frac{J}{K} \text{ or } \frac{J}{\text{mol K}}$$

Entropy is a measurement of energy dispersal in a system. The second law of thermodynamics states that energy in the universal tends to become more and more dispersed through spontaneous processes

- ✓ The second law of thermodynamics states that the entropy of the universe is always increasing.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

- This law gives us three conditions for ΔS_{total} :
 1. $\Delta S < 0$ (negative) ; your reaction is nonspontaneous
 2. $\Delta S = 0$ (zero) ; your reaction is at **equilibrium / reversible**
 3. $\Delta S > 0$ (positive) ; your reaction is spontaneous

The magnitude of ΔS_{total} is related to the idea of reversibility.

- A larger value of ΔS_{total} means it is difficult to reverse the reaction (backwards reaction is very non-spontaneous).
- A value of 0 for ΔS_{total} means the reaction is completely reversible and flows equally in both directions (in equilibrium).
- A negative value for ΔS_{total} means the reverse reaction is spontaneous.

Conceptual Entropy: Macroview

- Although not quite accurate scientifically, we tend to think of entropy as disorder. More disordered phases of matter are higher in entropy. This *can* help us conceptually:

- **We can easily see that the change in entropy (S) correlates with the change in phase:**

Solids (low entropy) < Liquids < Gases (high entropy)

- **Or with volume** (consider 1 mole of gas at room temperature)

10 L gas (lowest entropy) < 20 L gas < 50 L gas (highest entropy)

- **Or with temperature**

Gas at 100 K (lowest entropy) < gas at 500 K < gas at 1000 K (highest entropy)

Checkpoint Question

Identify the sign of ΔS_{sys} for each process listed below:

1. A sample of water is heated 12°C $+\Delta S$
2. A gas-phase reaction has a positive work value *compressing, $\Delta V < 0$, $\Delta n < 0$*
 $\Delta S = (-)$
3. A fixed number of gas molecules expand to a slightly greater volume $+\Delta S$
4. The deposition of carbon dioxide
 $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$ $\Delta S = (-)$

Conceptual Entropy: Microview

- The relationship between entropy and microstates is given by the formulas:

$$S = k \ln \Omega$$

$$S = k \ln x^i$$

Understand these
conceptually



- Entropy depends on the **complexity of the molecule**, represented by the orientations possible (x)
 - Larger molecules with diverse sets of bonds are more complex (higher entropy)
- Entropy depends on the total number of particles, represented by " i "
 - Having more particles (or more moles) leads to a higher entropy
- The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is 0 J/K.



Increasing Entropy

In summation, you can increase entropy based on:

1. Phase (going from solid to liquid [to aqueous] to gas)
2. Increasing volume (decreasing pressure)
3. Increasing temperature
4. Complexity of your molecule (a larger number of more diverse bonds)
5. Complexity of your solution **we don't really talk about this*
6. Increasing the number of particles

} Macro

} Micro

Entropy: Quantifying Entropy

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

- **Just like heat, change in entropy can be quantified with and without a temperature change.**

- The trick to understanding how to quantify entropy is understanding the equations from which it is derived. **The key here is understanding the units of entropy: J/K**

- **Entropy of a temperature change**

K.E.

$$q = mC_s \Delta T$$

If we integrate with respect to T to get entropy:

$$\Delta S = mC_s \ln \frac{T_f}{T_i}$$

→ Kelvin

- **Entropy of a phase change**

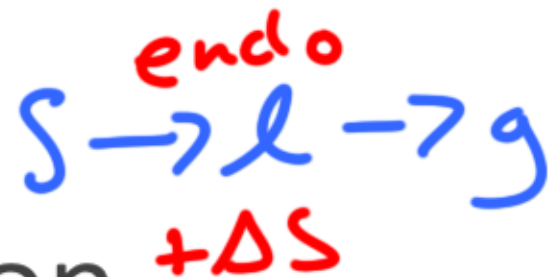
P.E.

$$q = \Delta H_{trans}$$

If we divide by the temperature we get:

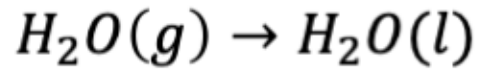
$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$





Big Picture Exam Question

Steam condenses into liquid water at 100°C:



What are the signs of:

1. $\Delta H = (-)$
2. $w = (+)$
3. $\Delta S_{\text{sys}} = (-)$
4. $\Delta S_{\text{surr}} = (+)$
5. $\Delta S_{\text{total}} = 0$
6. $\Delta T = 0$
7. $q = (-)$

Compression, $w > 0$, $-\Delta n$
 expansion, $w < 0$, $+\Delta n$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{surr}}}$$

$$\Delta S_{\text{total}} = \frac{\Delta H}{T_{\text{vap}}} + \frac{-\Delta H}{T_{\text{surr}}} \quad \left. \vphantom{\Delta S_{\text{total}}} \right\} \text{Rare}$$

$\swarrow \quad \searrow$
 $= 373.15 \text{ K}$

Calculation: Entropy of Heating

What is the ΔS for the heating of 20.0 grams of methanol ($C_s = 2.533 \text{ J / g K}$) from 34°C to 62°C ?

$$\begin{aligned}\Delta S &= m C_s \ln\left(\frac{T_f}{T_i}\right) \\ &= (20\text{g}) \left(2.533 \frac{\text{J}}{\text{g K}}\right) \ln\left(\frac{62 + 273.15}{34 + 273.15}\right) \\ &= 4.42 \frac{\text{J}}{\text{K}} \checkmark\end{aligned}$$

Calculation: Entropy of a Phase Change

$$\Delta S_{sys} = \frac{\Delta H}{T_{trans}}$$

The spontaneous condensation of bromine ($T_b = 332 \text{ K}$) at standard conditions is an exothermic reaction. What is the ΔS_{surr}° for this process? $\Delta H_{vap}^\circ = +31 \text{ kJ/mol}$ $\rightarrow \text{Br}_2(l) \rightarrow (g)$

Answer in J/mol K



$$\frac{-\Delta H_{sys}}{T_{surr}} = \frac{+31 \text{ kJ/mol}}{298.15 \text{ K}} = +0.10397 \frac{\text{kJ}}{\text{K}}$$

$$+104 \text{ J/K}$$

Reversible Heat and Entropy of Surroundings

According to the First Law, $q_{\text{sys}} = -q_{\text{surr}}$. However, based on the second law, ΔS_{sys} is **not** equal to $-\Delta S_{\text{surr}}$ for a spontaneous process.

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad \rightarrow \text{cold}$$

The spontaneous condensation of bromine ($T_b = 332 \text{ K}$) at room temperature is an exothermic reaction. Which of the following statements is/are true about this process?

i. $|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$

~~ii. $|\Delta S_{\text{sys}}| > |\Delta S_{\text{surr}}|$~~

iii. $T_{\text{trans}} > T_{\text{surr}}$ ✓

~~iv. $\Delta S_{\text{total}} < 0$~~

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad \leftarrow \text{“favorable”}$$

$(+)$ $(-)$ $(+)$

$$\frac{\Delta H}{T_{\text{trans}}} \quad \leftarrow \quad |\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}| \rightarrow \frac{-\Delta H}{T_{\text{surr}}}$$

$T_{\text{trans}} > T_{\text{surr}}$

There's a better way of looking at the spontaneity of a reaction system: Gibb's Free Energy

- **Gibb's Free Energy (G):** A state function derived to describe the stability of a system. For now, we are concerned most with the ΔG because of the conclusions we can make using its **sign** and **magnitude**.
- The change in free energy of a reaction (ΔG) is the capacity for a system to do work. By running a spontaneous reaction, you are lowering the free energy of the universe (helping the universe along its path of inevitable demise).

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

$$\Delta G_{rxn} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G < 0 \rightarrow \text{spont}$$

$$\Delta G = 0 \rightarrow \text{eq}$$

$$\Delta G > 0 \rightarrow \text{non-spont}$$