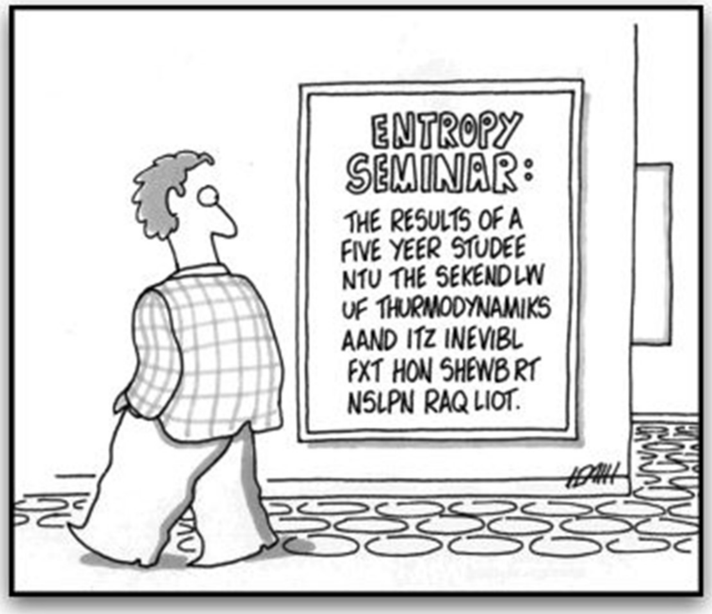
CHEM 202 Accelerated General Chemistry I — *TA: Alex Wang*
Week 7 – Thermodynamics IV — *October 7, 2021*
MERIT WS 7.2 — *Section AQG*



Review: Determining Heats of Reaction ΔH_{rxn}: Add all three methods to your Chemistry Toolbox!

Method I: Calorimetry

In a coffee cup calorimeter, 50.0 mL of 0.1000 M $AgNO_3$ and 50.00 mL of HCl are mixed. A precipitation reaction then ensues. If the two solutions were initially at 22.6°C and if the final temperature is 23.4°C, calculate the ΔH for the reaction in kJ/mol of AgCl formed. Assume a mass of 100 grams for the combined solution and a specific heat equal to that of water.

Method II: Hess' Law

Calculate ΔH for this reaction: $CH_4(g) + NH_3(g) \rightarrow HCN(g) + 3H_2(g)$ given:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ΔH = −91.8 kJ
$C(s) + 2H_2(g) \rightarrow CH_4(g)$ ΔH = −74.9 kJ
$H_2(g) + 2C(s) + N_2(g) \rightarrow 2HCN(g)$ ΔH = +270.3 kJ

Method III: Heats of Formation

$$\sum_{i}^{i=\infty} \boldsymbol{n_i \Delta H^{o}_{f,i}(products)} - \sum_{i}^{i=\infty} \boldsymbol{n_i \Delta H^{o}_{f,i}\,(reactants)}$$

Determine the ΔH_{rxn} of the following reaction using the data in Appendix 4.

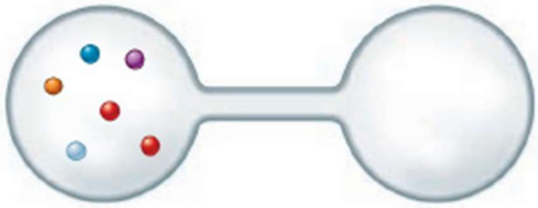
$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$

1. For the process A(*l*) → A(*g*), which direction is favored by changes in energy probability? Positional probability? Explain your answer. If you wanted to favor the process as written, would you raise or lower the temperature of the system? Explain.

2. Gas A_2 reacts with gas B_2 to form gas AB at constant temperature. The bond energy of AB is much greater than that of either reactant. What can be said about the sign of ΔH? ΔS_{surr}? ΔS? Explain how potential energy changes for this process. Explain how random kinetic energy changes during the process.

3. Predict the sign of Δ*S* for each of the following and explain.
    a. the evaporation of alcohol
    b. the freezing of water
    c. compressing an ideal gas at constant temperature
    d. heating an ideal gas at constant pressure
    e. dissolving NaCl in water

4. Consider the following illustration of six molecules of gas in a two-bulbed flask



    a. What is the most likely arrangement of molecules? How many microstates are there for this arrangement?
    b. Determine the probability of finding the gas in its most likely arrangement.

5. Which of the following involve an increase in the entropy of the system under consideration?
    a. melting of a solid
    b. mixing
    c. evaporation of a liquid
    d. separation
    e. sublimation
    f. diffusion
    g. freezing

6. Predict the sign of the entropy change and then calculate the standard state entropy values for the following reactions using Appendix 4.
    a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
    b. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

7. Why is an entropy change at a constant pressure greater than an entropy change at a constant volume for a gas? ***Think about the videos from 10/7 if you are stuck.

8. A 40-kg steel casting [C_p = 0.5 kJ/ (kg K)] at a temperature of 450°C is quenched with 150 kg of oil [C_p = 2.5 kJ/ (kg K)] at 25°C. If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

9. What is the smallest number of ice cubes at 0°C, each containing one mole of water, necessary to cool 500.0 g of liquid water initially at 20°C to 10°C at 1.00 atm? Assume for this problem that ΔH and C_p are temperature independent. Explain how ΔS of the system, surroundings, and universe change during this process.

   ΔH_f^0 = -285.6 kJ/mol of $H_2O(l)$
   ΔH_f^0 = -291.6 kJ/mol of $H_2O(s)$
   C_p = 75.3 J/mol·K for $H_2O(l)$
   C_p = 37.66 J/mol·K for $H_2O(s)$

10. You wake up early one morning to study thermodynamics, getting out your textbook, notes, and a laptop. You find an old 20 oz cola bottle that you almost fill with room temperature water for the day, and you seal the bottle. Your roommate gets up, sees you, wishes you luck, and hurries out for the day. You decide you want cooler water, so you place the sealed bottled in the freezer, and so intent on studying, you forget about it until hours later when you remove it from the freezer, now a block of ice in the bottle. You let the bottle sit on your desk and continue studying, forgetting about it once again until it once again becomes liquid water at room temperature. Your roommate comes back that evening, sees you at your desk with your textbook, notes, laptop, and sealed almost-filled bottle of room temperature water and says, “Well, it looks like nothing changed all day.” You look at your water bottle, look at your text and see it turned to Section 10.5 “Entropy and the Second Law of Thermodynamics.” You smile and say, “Oh, hasn’t it?”
    a. Let’s consider the system to be the water in the sealed bottle that started and ended at room temperature (but that you neglected to drink it all). Due to what happened to the water, how, if at all, do each of the following: ΔS, ΔS_{surr}, and ΔS_{univ} change (do each increase, decrease, or stay the same)? Explain why. Answer this for each step of what happened to the water and the overall. Full credit is reserved for a complete, coherent, conceptual explanation, which discusses signs and relative magnitudes.

b. You added 566 mL of water at 25°C (also your constant room temperature) and your freezer was set to -2°C. Assume the water was on the freezer long enough to reach thermal equilibrium with the freezer, and that the heat capacities of water and ice do not change over temperature range in question. Use the following data to calculate ΔS, ΔSsurr, and ΔSuniv due to what happens with the water. Report your answers in J/K for the overall process of starting and ending with room temperature water. Show all of your work and explain the significance of the results.

Density of water at 25 degrees Celsius: 1.00 g/mL
Cp for H_2O (l) = 75.3 J/mol K
Cp for H_2O (s) = 37.6 J/mol K
ΔH_{fusion} for H_2O(l) at 0°C = 6.010 kJ/mol

11. Heat engines like the Carnot, Otto, Diesel, or Kalina cycles function off the basis of the Clausius Inequality, an extension of the second law of thermodynamics that applies to the whole universe. It is stated as the following cyclic integral on the left of the arrow and evaluation of the integral leads to the simplified expression on the right of the arrow.

$$\oint \frac{dQ}{T} \leq 0 \rightarrow dS^{sys} - \frac{dq^{sys}}{T} \geq 0$$

ONLY CONSIDERING THE EXPRESSION ON THE RIGHT, what does this mean physically? Explain this in terms of heat transferred and entropy of the system. (Hint: Integrate both sides of the expression if you need a more 'finite' picture!) Why is the inequality symbol important in relation to the second law of thermodynamics? In the first law of thermodynamics, why do we use an equal's sign to represent the relationship between the TOTAL energy at the beginning of a process and the TOTAL energy at the end? Why is this distinction important?

12. The enthalpy of neutralization for the reaction of a strong acid with a strong base is -56 kJ/mole of $H_2O(l)$ produced. How much energy will be released when 200.0 mL of 0.400 M nitric acid is mixed with 150.0 mL of 0.5 M potassium hydroxide? If both solutions are originally at 25°C, what is the final temperature of the mixture?