CH 301 Exam 4 Review Session - Discussion Questions

Adapted from McCord gchem additional content spring 2022

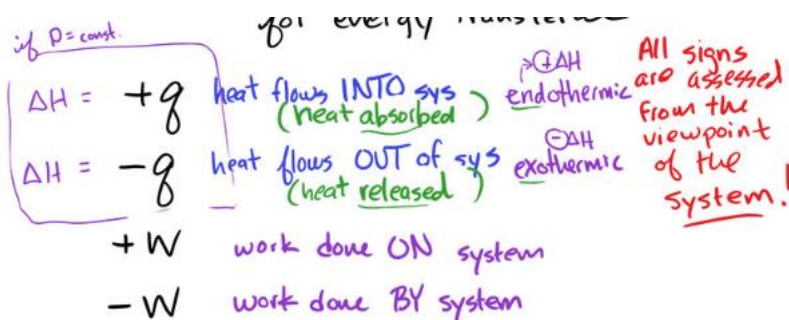**State Function / Path Function**

Is temperature, T, a state function? Give an example of a state function.

Temperature is a state function. Another state function is volume, V or internal energy, U.

System vs. Surroundings

Draw out two diagrams of system and surroundings

Give an example of negative q and an example of positive q.

Work

Suppose a gas compresses by 185 mL against a pressure of 0.400 atm. How much work is done on the system due to this compression? Report your answer in units of Joules.

$$w = -P_{ext}\Delta V$$
$$P_{ext} = 0.400 atm$$
$$\Delta V = -185 mL = -0.185 L$$
$$w = -(0.4 atm)(-0.185 L)$$
$$w = 0.074 \cdot atm \times \frac{101.325 J}{1 L \cdot atm} = 7.50 J$$

Heat

Which of the following materials would you expect to experience the greatest temperature change if 1 gram of each metal were exposed to the same amount of thermal energy? Explain your answer.

Aluminum 0.89 J/g °C
Lead 0.129 J/g °C°
Steel 0.466 J/g °C

Lead would heat up the fastest of the three materials listed. Lead has the lowest specific heat capacity. This means that it takes less energy to raise the temperature of 1 gram of lead by 1 degree Celsius compared to aluminum or steel. Therefore, if they are each exposed to the same amount of thermal energy, then lead will experience the greatest temperature change of the three materials.

Internal Energy
A system lost 11.9 J of heat, yet it was found that its internal energy increased by 85.5 J. Calculate w. Was work done on the system or did the system do work?

The system lost heat. The sign of q should be negative. Internal energy increases, which means the sign of ΔU should be positive.

$$\Delta U = q + w$$
$$q = -11.9 J$$
$$\Delta U = +85.5 J$$
$$+85.5 J = -11.9 J + w$$
$$w = +97.4 J$$

Endothermic / Exothermic
Which types of phase changes are endothermic? Which types of phase changes are exothermic? Give an example of a common chemical process that is exothermic.

Endothermic Phase Changes: Melting (fusion), Boiling, Sublimation Exothermic Phase Changes: Freezing, Condensation, Deposition (solidification) Combustion is a common exothermic chemical process.

Coffee Cup Calorimetry
When 0.113 g of liquid benzene, C6H6, burns in excess oxygen in a calibrated constant pressure calorimeter the temperature of the calorimeter rises by 8.60°C and carbon dioxide gas and liquid water are formed.
Given that the heat capacity of the calorimeter is 551 J/°C, calculate the amount of energy that flowed from the system to the surroundings?

Balanced Chemical Equation:

$$2C_6H_6 \ (l) + 15O_2 \ (g) \rightarrow 12CO_2 \ (g) + 6H_2O \ (l) + heat$$

$$q_p = q_{cal} = C_{cal}\Delta T_{cal}$$
$$q_p = q_{cal} = (551\tfrac{J}{°C})(8.60°C)$$
$$q_p = 4738.6 \ J = 4.7386 \ kJ \approx 4.74 \ kJ$$

Heat flow at constant pressure is defined as change in enthalpy or ΔH. Calculate the change in enthalpy of the combustion per mole of liquid benzene using the data given.

$$q_{system} = -q_{surroundings}$$
$$q_{system} = -4.7386 \ kJ$$

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$$0.113g \ C_6H_6 \times \frac{1mol \ C_6H_6}{78g \ C_6H_6} = 1.45 \times 10^{-3} mol \ C_6H_6$$

Bomb Calorimetry

1.14 g of liquid octane (C8H18) is combusted in a bomb calorimeter surrounded by 1 L of water. The combustion produces carbon dioxide gas and liquid water. The initial temperature of the water and calorimeter hardware is 25˚C. The final temperature of the water and calorimeter hardware is 33˚C. The heat capacity of the calorimeter (not including the water!) is 456 J/˚C. Determine the heat flow into the surroundings (water + calorimeter). Recall that the density of water is 1 g/mL.

$$\Delta U_{combustion} = q_v = q_{system} = -q_{surroundings}$$

$$q_{surroundings} = m_{water} C_{s,water} \Delta T_{water} + C_{calorimeter} \Delta T_{calorimeter}$$

$$q_{surroundings} = m_{water} C_{s,water} \Delta T_{water} + C_{calorimeter} \Delta T_{calorimeter}$$

$$\Delta T_{water} = \Delta T_{calorimeter}$$

$$q_{surroundings} = \left(m_{water} C_{s,water} + C_{calorimeter} \right)\left(T_{final} - T_{initial} \right)$$

$$m_{water} = \rho_{water} V_{water} = \left(1 \tfrac{g}{mL} \right)(1000mL) = 1000g$$

$$q_{surroundings} = \left((1000g)(4.184 \tfrac{J}{g°C}) + 456 \tfrac{J}{°C} \right)(33°C - 25°C)$$

$$q_{surroundings} = (4640 \tfrac{J}{°C})(8°C)$$

$$q_{surroundings} = 37120 \ J \approx 37.1kJ$$

From the data, determine the change in internal energy of octane per mole combusted.

$$q_{system} = -q_{surroundings}$$
$$q_{system} = -37.12 \ kJ$$

$$\Delta U_{combustion} = q_v = q_{system} = -q_{surroundings}$$
$$\Delta U_{combustion} = -37.12 \ kJ$$

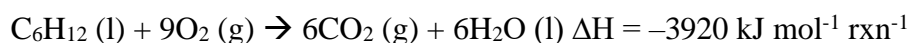$$1.14g \ C_8H_{18} \times \frac{1mol \ C_8H_{18}}{114g \ C_8H_{18}} = 0.01mol \ C_8H_{18}$$

$$\Delta U_{n,combustion} = \frac{\Delta U_{combustion}}{n_{C_8H_{18}}}$$

$$\Delta U_{n,combustion} = \frac{-37.12\ kJ}{0.01 mol\ C_8H_{18}}$$

$$\Delta U_{n,combustion} = -3712\ \tfrac{kJ}{mol} \approx -3.71 \times 10^3\ \tfrac{kJ}{mol}$$

Enthalpy

Here is a thermochemical equation for the combustion of cyclohexane at room temperature:

$$C_6H_{12}\ (l) + 9O_2\ (g) \rightarrow 6CO_2\ (g) + 6H_2O\ (l)\ \Delta H = -3920\ kJ\ mol^{-1}\ rxn^{-1}$$
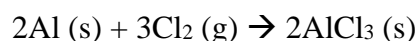
What would happen to the value of the enthalpy if you reversed the chemical process (switched reactants and products)? What would happen to the value of the enthalpy if you reduced each of the stoichiometric coefficients by a factor of 3?
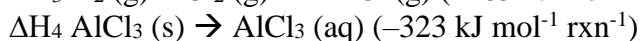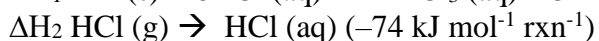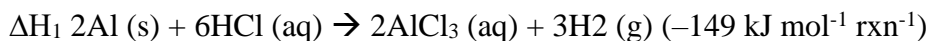
If you reversed the process, the products and reactants would switch places and the sign of ΔH would change (the magnitude of the value would remain the same). If you reduced each of the stoichiometric coefficients by a factor of 3, the value of ΔH would also reduce by a factor of three.

Hess's Law

Show how you would manipulate the listed thermochemical equations to get the desired reaction for the synthesis of anhydrous aluminum chloride, which is written:
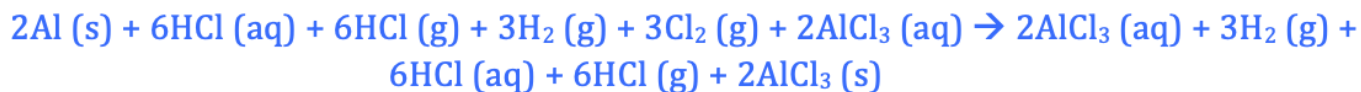
$$2Al\ (s) + 3Cl_2\ (g) \rightarrow 2AlCl_3\ (s)$$

Determine the enthalpy of reaction.

ΔH_1 $2Al\ (s) + 6HCl\ (aq) \rightarrow 2AlCl_3\ (aq) + 3H_2\ (g)$ ($-149\ kJ\ mol^{-1}\ rxn^{-1}$)
ΔH_2 $HCl\ (g) \rightarrow HCl\ (aq)$ ($-74\ kJ\ mol^{-1}\ rxn^{-1}$)
ΔH_3 $H_2\ (g) + Cl_2\ (g) \rightarrow 2HCl\ (g)$ ($-185\ kJ\ mol^{-1}\ rxn^{-1}$)
ΔH_4 $AlCl_3\ (s) \rightarrow AlCl_3\ (aq)$ ($-323\ kJ\ mol^{-1}\ rxn^{-1}$)

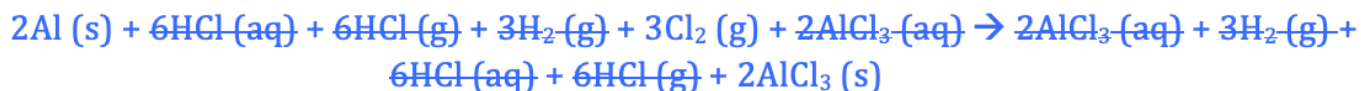**$2AlCl_3\ (aq) \rightarrow 2AlCl_3\ (s)$ $\Delta H_4 = +646\ kJ\ mol^{-1}rxn^{-1}$**

Observe that the change in enthalpy for reaction 4 increased in magnitude by a factor of two and changed signs from negative to positive.

Now we can "add up" the equations and their ΔH values. If we manipulated our equations well, the net result should match our desired equation:

$$2Al\ (s) + 6HCl\ (aq) \rightarrow 2AlCl_3\ (aq) + 3H_2\ (g) \qquad \Delta H_1 = -149\ \text{kJ mol}^{-1}\text{rxn}^{-1}$$

$$6HCl\ (g) \rightarrow 6HCl\ (aq) \qquad \Delta H_2 = -444\ \text{kJ mol}^{-1}\text{rxn}^{-1}$$

$$3H_2\ (g) + 3Cl_2\ (g) \rightarrow 6HCl\ (g) \qquad \Delta H_3 = -555\ \text{kJ mol}^{-1}\text{rxn}^{-1}$$

$$+ \qquad 2AlCl_3\ (aq) \rightarrow 2AlCl_3\ (s) \qquad \Delta H_4 = +646\ \text{kJ mol}^{-1}\text{rxn}^{-1}$$

$$2Al\ (s) + 6HCl\ (aq) + 6HCl\ (g) + 3H_2\ (g) + 3Cl_2\ (g) + 2AlCl_3\ (aq) \rightarrow 2AlCl_3\ (aq) + 3H_2\ (g) + 6HCl\ (aq) + 6HCl\ (g) + 2AlCl_3\ (s)$$

Cross out the compounds that show up on both sides (remember HCl (l) and HCl (aq) will cancel one another out for this problem):

$$2Al\ (s) + \cancel{6HCl\ (aq)} + \cancel{6HCl\ (g)} + \cancel{3H_2\ (g)} + 3Cl_2\ (g) + \cancel{2AlCl_3\ (aq)} \rightarrow \cancel{2AlCl_3\ (aq)} + \cancel{3H_2\ (g)} + \cancel{6HCl\ (aq)} + \cancel{6HCl\ (g)} + 2AlCl_3\ (s)$$

Write the net equation:

$$2Al\ (s) + 3Cl_2\ (g) \rightarrow 2AlCl_3\ (s)$$

Entropy
Give two examples of processes that are spontaneous at room temperature and pressure – provide one physical change and one chemical change

Physical processes: Dropping a book, dry ice subliming, ice melting
Chemical processes: Iron rusting, some combustion reactions

Which compound would you expect to have the lowest absolute entropy of the given pairs? Explain your choice.

a. Br_2 (l) or Br_2 (g)?
Bromine liquid has a lower absolute entropy because gases have greater positional disorder than their liquid phases.

b. C (s) graphite or C (s) diamond?
Diamond has a lower absolute entropy. A simpler structure than graphite and can form a more perfect crystal than graphite. Diamond is comprised of tetrahedral carbon atoms covalently bonded to other tetrahedral carbon atoms. Graphite is comprised of sheets of trigonal planar carbons bonded together in rings and the sheets are held together by IMFs.

c. Fe_2O_3 (s) or Fe_3O_4 (s)?
Iron (III) oxide (Fe_2O_3) has a lower absolute entropy because it has fewer atoms to arrange. This gives Fe_2O_3 lower positional disorder than Fe_3O_4

d. NH_3 (g) or NH_3 (aq)?

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Aqueous ammonia has a lower absolute entropy than gaseous ammonia. When dissolved in water, the interactions between ammonia and water give the ammonia lower positional disorder than gaseous ammonia.

Gibbs Free Energy

The change in the Gibb's free energy, ΔG, is actually derived from the change in entropy of the universe. What is the equation relating the change in Gibb's free energy for a process and the change in enthalpy and entropy for the same process? Define the variables and provide units for each.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

ΔG is the change in Gibb's free energy and it usually has units of kilojoules (kJ) or kilojoules per mole (kJ/mol). ΔH is the change in enthalpy and it usually has units of kilojoules (kJ) or kilojoules per mole (kJ/mol). T is absolute temperature in units of Kelvin (K). ΔS is the change in entropy and it usually has units of joules per Kelvin (J/K) or joules per mole per Kelvin (kJ/molK). Make sure to convert joules to kilojoules!

What is the sign of ΔG for a spontaneous process? For a non-spontaneous process?

The sign of ΔG is negative when a process is spontaneous. The sign of ΔG is positive when a process is non-spontaneous.

What are the four possible combinations of ΔH and ΔS and what kind of change do they lead to – always spontaneous, always non-spontaneous or temperature dependent?

Calculate the ΔG_{rxn} of the following reaction using the given standard free energy of formation data:

$6CO_2$ (g) + $6H_2O$ (l) → $C_6H_{12}O_6$ (s) + $6O_2$ (6)
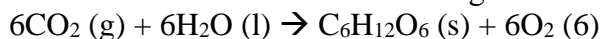
$\Delta G_f °$ CO_2 (g) $= -394.36$ kJ/mol

$\Delta G_f °$ H_2O (l) $= -237$ kJ/mol

$\Delta G_f °$ $C_6H_{12}O_6$ (s) $= -910$ kJ/mol

$$\Delta G_{rxn} = \sum n\Delta G^\circ_{f,prod.} - \sum n\Delta G^\circ_{f,react.}$$

$$\Delta G_{rxn} = \left[1\Delta G^\circ_{f,C_6H_{12}O_6} + 6\Delta G^\circ_{f,O_2}\right] - \left[6\Delta G^\circ_{f,H_2O} + 6\Delta G^\circ_{f,CO_2}\right]$$

$$\Delta G_{rxn} = \left[1(-910\tfrac{kJ}{mol}) + 6(0\tfrac{kJ}{mol})\right] - \left[6(-237\tfrac{kJ}{mol}) + 6(-394.36\tfrac{kJ}{mol})\right]$$

$$\Delta G_{rxn} = (-910\tfrac{kJ}{mol}) - (-3788.16\tfrac{kJ}{mol})$$

$$\Delta G_{rxn} = -1183.08\tfrac{kJ}{mol} + 3788.16\tfrac{kJ}{mol}$$

$$\Delta G_{rxn} = +2878.16\tfrac{kJ}{mol\ rxn}$$

The condensation of CH_3OH gas to CH_3OH liquid is spontaneous when ΔG is negative. Using the data below, predict at what temperature is this process first spontaneous at 1 bar.

S° CH3OH (g) = 240 J/K mol   ΔHf ° CH3OH (g) = –201 kJ/mol
S° CH3OH (l) = 127 J/K mol   ΔHf ° CH3OH (l) = –239 kJ/mol

$$CH_3OH(g) \rightarrow CH_3OH(l)$$

$$\Delta H_{rxn} = \sum n\Delta H^\circ_{f,prod.} - \sum n\Delta H^\circ_{f,react.}$$

$$\Delta H_{rxn} = \left[2\left(\Delta H^\circ_{f,CH_3OH(l)}\right)\right] - \left[1\left(\Delta H^\circ_{f,CH_3OH(g)}\right)\right]$$

$$\Delta H_{rxn} = \left[1\left(-239\tfrac{kJ}{mol}\right)\right] - \left[1\left(-201\tfrac{kJ}{mol}\right)\right]$$

$$\Delta H_{rxn} = -39\tfrac{kJ}{mol}$$

$$\Delta S_{rxn} = \sum nS^\circ_{prod.} - \sum nS^\circ_{react.}$$

$$\Delta S_{rxn} = \left[1\left(S^\circ_{CH_3OH(l)}\right)\right] - \left[1\left(S^\circ_{CH_3OH(g)}\right)\right]$$

$$\Delta S_{rxn} = \left[1(127\tfrac{J}{K\cdot mol})\right] - \left[1\left(240\tfrac{J}{K\cdot mol}\right)\right]$$

$$\Delta S_{rxn} = -113\tfrac{J}{K\cdot mol}$$

$$\Delta S_{rxn} = -0.113\tfrac{kJ}{K\cdot mol} \quad <--\ Units!$$

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

$$\Delta H_{rxn} = -39\tfrac{kJ}{mol}$$

$$\Delta S_{rxn} = -0.113\tfrac{kJ}{K\cdot mol}$$

$$0 = -39\tfrac{kJ}{mol} - (T)(-0.113\tfrac{kJ}{K\cdot mol})$$

$$39\tfrac{kJ}{mol} = (T)(0.113\tfrac{kJ}{K\cdot mol})$$

$$\frac{39\tfrac{kJ}{mol}}{0.113\tfrac{kJ}{K\cdot mol}} = T_{Condensation}$$

$$345K = T_{Condensation} \ ...\ Spont\ when\ T < 345K$$