

# Thermo3Key

Wednesday, November 16, 2016 9:58 AM

## Concepts and Problems from the First Law of Thermodynamics.

1. Define the First and Second Laws of Thermodynamics in words and with an equation. Discuss how they are related to our understanding on  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ .

1st Law - energy must be conserved  $\Delta U_{\text{sys}} = -\Delta U_{\text{surr}} \leftarrow \Delta H \text{ comes from the 1st law}$   
( $\Sigma = \Delta H @ \text{constant } p$ )

2nd Law - the universe tends toward disorder  $\Delta S_{\text{univ}} > 0 \rightarrow \Delta G = -T\Delta S_{\text{univ}}$

2. Standard molar entropy ( $S^\circ$ ) can be used to calculate reaction entropies. These values are always positive ( $S^\circ > 0$ ). Why?

3rd law says that entropy must exist, so everything MUST have some disorder

3. For each pair, predict which molecule will have a higher molar entropy:

CO vs.  $\text{CO}_2$  (both are gases at 100 °C)     $\text{H}_2\text{O}$  (s) vs.  $\text{H}_2\text{O}$  (l)     $\text{CH}_4$  (g) at 25 °C vs.  $\text{CH}_4$  (g) at 250 °C

larger molecule

liquid is more disordered than solid

higher Temp

4. In class, we discussed that one example of the relationship between  $\Delta U$ ,  $q$ , and  $w$  is a car engine. The system is represented by the car itself – the total internal energy is determined by how much gas you have in the tank. As you drive the car, work being done to move the car and the engine is getting hot – together, these are the two ways that the internal energy of the system is being transferred to the surroundings.

Now it's your turn, think about the human body. The food that you eat is your energy. Describe how your body gets rid of that energy and relate it back to  $\Delta U = q + w$ .

food intake is converted to energy – this is  $U \rightarrow$  total internal energy  
 $U$  can be depleted in two ways: heat leaving (yes, we are hotter than the surroundings)  
or by doing something active (like running) – this is work

5. When thinking about the heat of a reaction,  $q$  and  $\Delta H$  can be used interchangeably in most cases.

- a. Why? Pressure at the atmosphere won't change, so  $p$  is constant
- b. What must be true if  $q \neq \Delta H$ ?

the pressure has changed

6. If 100 mL of liquid water is cooled from 98 °C to 25 °C:

- a. Is the reaction endothermic or exothermic?
- b. What is the sign of  $\Delta H$ ?  $\Delta H < 0$
- c. What is the sign of  $\Delta S$ ?  $\Delta S < 0$  (hot  $\rightarrow$  cold)
- d. The heat capacity of liquid water is  $4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ . Calculate  $\Delta H$ . Recall that the density of water is  $1 \text{ g/mL}$ .

$$\frac{100 \text{ mL} | 1 \text{ g}}{1 \text{ mL}} = 100 \text{ g}$$

$$q = 100 \text{ g} \left( \frac{4.184 \text{ J}}{\text{g } ^\circ\text{C}} \right) (25^\circ\text{C} - 98^\circ\text{C})$$

$$q = -30543.2 \text{ J} = -30.5432 \text{ kJ}$$

$$q = \Delta H$$



7. Octane ( $C_8H_{18}$ ) has a melting temperature of  $-57.1^\circ C$  and a boiling temperature of  $125.1^\circ C$ .

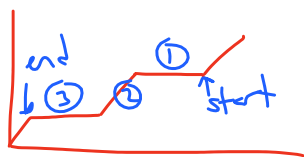
a.  $\Delta H_{vap}$  for octane is  $36.3 \text{ kJ/mol}$ . Calculate  $\Delta S_{vap}$ . Hint: remember that  $\Delta G = 0$  at the phase change temperature.

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

$$0 = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H}{T} = \frac{36.3 \text{ kJ/mol}}{(125.1^\circ C + 273.15)} = 0.091 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} = 91 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

b. If exactly  $12.2 \text{ g}$  of octane vapor at  $125.1^\circ C$  is cooled to a solid at the melting temperature, calculate  $\Delta H$ .  $\Delta H_{fus} = 21.75 \text{ kJ/mol}$   $C_{liquid} = 255.68 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$ . All other info is above.



\* note  $\rightarrow \Delta H_{fus}$  refers to  $S \rightleftharpoons L$ , but we are going from  $L \rightleftharpoons S$ , so use  $-\Delta H_{fus}$

- same with  $\Delta H_{vap}$ , use  $-\Delta H_{vap}$  because we are reversing the reaction

$$\frac{12.2 \text{ g}}{114.26 \text{ g}} \frac{\text{mol}}{\text{mol}} = 0.107 \text{ mol}$$

$$\textcircled{1} \quad q = 0.107 \text{ mol} \left( -36.3 \frac{\text{kJ}}{\text{mol}} \right) = -3.88 \text{ kJ}$$

$$\textcircled{2} \quad q = 0.107 \text{ mol} \left( 255.68 \frac{\text{J}}{\text{mol}\cdot^\circ\text{C}} \right) (-57.1^\circ\text{C} - 125.1^\circ\text{C})$$

$$q = -4984.6 \text{ J} \frac{1 \text{ kJ}}{10^3 \text{ J}} = -4.984 \text{ kJ}$$

$$\textcircled{3} \quad q = 0.107 \text{ mol} \left( -21.75 \frac{\text{kJ}}{\text{mol}} \right) = -2.33 \text{ kJ}$$

$$\text{Total} = q_1 + q_2 + q_3 = -3.88 \text{ kJ} + -4.984 \text{ kJ} + -2.33 \text{ kJ}$$

$$\Delta H = q_{\text{tot}} = -11.19 \text{ kJ}$$

8. Consider the sublimation of sodium metal:  $\text{Na}(s) = \text{Na}(g)$

a. Write an equilibrium constant for this reaction.

$$K = P_{\text{Na}} \quad \text{or} \quad K = [\text{Na}(g)]$$

b. Predict the sign of  $\Delta H$  and  $\Delta S$ . Clearly explain why you made these selections

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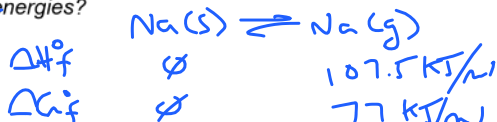
$\Delta H > 0$  - breaking IMF

$\Delta S > 0$  - gases are more disordered than solids

c. Will this reaction be spontaneous at high temperatures, low temperatures, both, or neither?

- need high T for  $\Delta G < 0$

d. Noting that  $\Delta H_f^\circ = 107.5 \text{ kJ mol}^{-1}$  and  $\Delta G_f^\circ = 77.0 \text{ kJ mol}^{-1}$  for Na (g), determine  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for this reaction. Hint: what is special about Na(s) and what does that mean about the formation energies?



$$\Delta H^\circ = 107.5 \text{ kJ/mol} - \emptyset = 107.5 \text{ kJ/mol}$$

$$\Delta G^\circ = 77 \text{ kJ/mol} - \emptyset = 77 \text{ kJ/mol}$$

e. From this information, calculate the sublimation temperature of sodium. Hint: remember that  $\Delta G = 0$  at the phase change temperature.

$$0 = \Delta H - T\Delta S$$

$$77 = 107.5 - 298.15 \Delta S$$

$$\Delta S^\circ = 0.1023 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$$

$$T = \frac{\Delta H}{\Delta S} = \frac{107.5 \text{ kJ/mol}}{0.1023 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}} = 1050.8 \text{ K}$$

$$\text{or } 777.8^\circ \text{C}$$

f. Calculate the equilibrium constant for this reaction.

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -31.06$$

$$77,000 \text{ J/mol} = -8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298.15 \text{ K}) \ln K$$

$$K = 3.23 \times 10^{-14}$$

g. What pressure of sodium is needed for equilibrium to be established?

$$3.23 \times 10^{-14} \text{ atm}$$

h. If the pressure of Na (g) is  $5 \times 10^{-10}$  atm, will the equilibrium shift to make more gas or solid?

$Q > K$  reactants will be made

i. The heat capacity of Na(s) is  $1.214 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ . If a block of Na (s) at  $350^\circ \text{C}$  is placed in 300 mL of mineral oil (density =  $0.85 \text{ g/mL}$  and  $C = 1.67 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ ) at  $20^\circ \text{C}$  and the final temperature is found to be  $32^\circ \text{C}$ , what was the mass of sodium?

$$q_{\text{Na}} = -q_{\text{oil}}$$

$$\frac{300 \text{ mL} \times 0.85 \text{ g}}{\text{mL}} = 255 \text{ g}$$

$$m \left( 1.214 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (32^\circ\text{C} - 350^\circ\text{C}) = -255 \text{ g} \left( 1.67 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (32 - 20)$$

$$-386.05 m = -5110.2$$

$$m = 13.24 \text{ g}$$

9. The combustion of octane produces -5.53 MJ/mol of heat. If 100 g of octane is combusted, how much water at 25 °C can be boiled?

This is a big problem – let's walk through it stepwise:

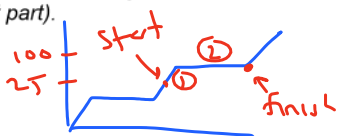
Determine how much heat is produced when 100 g of octane is combusted. You'll need a balanced equation, the moles of octane, and use  $\Delta H$  as a conversion factor to figure out the enthalpy for this reaction.



$$\Delta H = \frac{-5.53 \text{ MJ}}{\text{mol}} = \frac{-5.53 \text{ MJ}}{2 \text{ mol C}_8\text{H}_{18}}$$

$$\frac{100 \text{ g}}{114.26 \text{ g/mol}} = 0.875 \text{ mol C}_8\text{H}_{18} \left| \frac{-5.53 \text{ MJ}}{2 \text{ mol C}_8\text{H}_{18}} \right. = -2.42 \text{ MJ}$$

Ok, now figure out how much the heat that it would take exactly one mole of  $\text{H}_2\text{O}$  to be heated from a liquid at 25 °C to a gas at the boiling temperature. Do this in two steps: 1. How much heat to boil 1 mole of water? 2. How much heat to increase the temperature from 25°C to 100 °C?  $\Delta H_{\text{vap}}$  of water is 40.65 kJ/mol and in a previous problem, you learned that the heat capacity of liquid water is 4.184 J g<sup>-1</sup> °C<sup>-1</sup>. Your answer to this part will be in J per 1 mol (which we can use as a conversion factor for the next part).



$$\textcircled{1} \frac{1 \text{ mol}}{18.02 \text{ g/mol}} = 18.02 \text{ g} \quad Q = 18.02 \text{ g} \left( \frac{4.184 \text{ J}}{\text{g} \cdot \text{C}} \right) (100 - 25)$$

$$Q_1 = 5654.7 \frac{\text{J}}{\text{mol}}$$

$$\textcircled{2} \frac{40.65 \text{ kJ}}{1 \text{ mol}} \dots \text{done}$$

$$\text{Total: } \frac{5.654 \text{ kJ}}{1 \text{ mol}} + \frac{40.65 \text{ kJ}}{1 \text{ mol}}$$

46.3 kJ needed for 1 mol of  $\text{H}_2\text{O}$

Ok, from the 1<sup>st</sup> part, you found out how much energy is produced and the second part you learned how much energy is needed for exactly one mole. Now use the answer to the 2<sup>nd</sup> part as a conversion factor to convert the first answer to moles.

$$2.42 \text{ MJ available} = 2420 \text{ kJ}$$

$$46.3 \text{ kJ needed for 1 mol} \quad \frac{2420 \text{ kJ}}{46.3 \text{ kJ}} \left| \frac{1 \text{ mol}}{1} \right. = 52.27 \text{ mol H}_2\text{O}$$

$$\frac{52.27 \text{ mol}}{1} \left| \frac{18.02 \text{ g}}{\text{mol}} \right. = 941.9 \text{ g or } 941.9 \text{ ml of H}_2\text{O}$$