

# Chemistry 217/Quiz I

November 24, 11

75 minutes

## KEY

Name: \_\_\_\_\_

ID#: \_\_\_\_\_

Signature: \_\_\_\_\_

### Useful Information

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

$$\gamma = C_p / C_v$$

Q #	Points
1	/15
2	/15
3	/20
4	/15
5	/15
6	/20

**Total:** \_\_\_\_\_ %

1. (15%) A 1.000 g sample of octane ( $C_8H_{18}$ ) is burned in a bomb calorimeter containing 1200 grams of water at an initial temperature of  $25.00^\circ C$ . After the reaction, the final temperature of the water is  $33.20^\circ C$ . The heat capacity of the calorimeter (also known as the “calorimeter constant”) is  $837 J/^\circ C$ . The specific heat of water is  $4.184 J/g^\circ C$ . Calculate  $\Delta E$  and  $\Delta H$  of combustion of octane in  $kJ/mol$ .

Since this is a combustion reaction, heat flows from the system to the surroundings... thus, it is exothermic. The heat released by the reaction will be absorbed by two things: (a) the water in the calorimeter and (b) the calorimeter itself.

a. Calculate the heat absorbed by the water ( $q_{water}$ )

$$\begin{aligned}m &= 1200 \text{ grams} \\c_{water} &= 4.184 J/g^\circ C \\ \Delta T &= 33.20 - 25.00 = 8.20^\circ C\end{aligned}$$

$$\begin{aligned}q_{water} &= (m)(c)(\Delta T), \text{ so} \\ q_{water} &= (1200 \text{ g})(4.184 \frac{J}{g \cdot ^\circ C})(8.20^\circ C) = 41170.56 \text{ J} = \mathbf{41.2 \text{ kJ}}\end{aligned}$$

b. Calculate the heat absorbed by the calorimeter ( $q_{cal}$ )

The temperature change of the calorimeter is the same as the temperature change for water. In this step, however, we must use the **heat capacity** of the calorimeter, which is already known. When using heat capacity, the mass of the calorimeter is not required for the calculation. (It's already incorporated into the heat capacity).

$$\begin{aligned}C_{cal} &= 837 J/^\circ C \\ \Delta T &= 33.20 - 25.00 = 8.20^\circ C\end{aligned}$$

$$\begin{aligned}q_{cal} &= (C_{cal})(\Delta T), \text{ so} \\ \text{so, } q_{cal} &= (837 \frac{J}{^\circ C})(8.20^\circ C) = 6863.4 \text{ J} = \mathbf{6.86 \text{ kJ}}\end{aligned}$$

The TOTAL heat absorbed by the water and the calorimeter is the sum of (a) and (b):  $41.2 + 6.86 = \mathbf{+48.1 \text{ kJ}}$ . (Remember,  $q$  is positive because the heat is being absorbed).

The amount of heat released by the reaction is equal to the amount of heat absorbed by the water and the calorimeter. We just need to change the sign. So,

$$\boxed{q_{reaction} = -48.1 \text{ kJ}}$$

Since 1.000 gram of octane was burned, the **heat of combustion** for octane is equal to  $-48.1 \text{ kJ/gram}$ . In other words, when one mole of octane is burned,  $48.1 \text{ kJ}$  of heat is released from the reaction. *What is the heat of combustion in  $kJ/mol$ ?*

$$1 \text{ mol of octane weighs } 114 \text{ grams, so } (-48.1 \text{ kJ/g})(114 \text{ g/mol}) = \mathbf{-5483 \text{ kJ/mol.}}$$

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + RT\Delta(n_{gas})$$

2. (15%) For a gas following

$$p(V-b) = RT$$

a. Derive the expression for the Joule-Thomson coefficient  $\mu_{JT}$ .

$$p(V-b) = RT \rightarrow V = \frac{RT}{p} + b \rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$$

$$\mu_{JT} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{T\left(\frac{R}{p}\right) - V}{C_p} = \frac{b}{C_p} < 0$$

$$\text{On the other hand, } \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{\Delta T}{\Delta p}$$

b. When the pressure drops in a Joule-Thomson expansion for such a gas, what is the sign of  $\Delta T$ ?

Expansion  $\Rightarrow \Delta P < 0 \Rightarrow \Delta T < 0 \Rightarrow$  gas will cool down as it expands

3. (20%) Consider the cooling of 1.00 mol of  $O_2$  (g) from 298K to  $O_2$  (l) at 90.19K. Given:  $\Delta_{\text{vap}}H$  (90.19K) = 6820  $J\text{mol}^{-1}$  and  $C_p = 7R/2$ .

a. What are  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{sur}}$ , and  $\Delta S_{\text{universe}}$  if the process is done reversibly?

$$O_2(g, 298K) \xrightarrow[\Delta S_1]{\Delta H_1} O_2(g, 90.19K) \xrightarrow[\Delta S_2]{\Delta H_2 = -\Delta_{\text{vap}}H} O_2(l, 90.19K)$$

$$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2 = C_p \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_2}{T_1} = \frac{7}{2} R \ln\left(\frac{T_2}{T_1}\right) - \frac{\Delta H_{\text{vap}}}{T_1}$$

$$\Rightarrow \Delta S_{\text{sys}} = \frac{7}{2} (8.314) \ln\left(\frac{90.19}{298}\right) - \frac{6820}{90.19} \Rightarrow \Delta S_{\text{sys}} = -110.4 JK^{-1}$$

$$\Delta S_{\text{univ}} = 0 \text{ (reversible)} \Rightarrow \Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = 110.4 JK^{-1}$$

b. What are  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{sur}}$ , and  $\Delta S_{\text{universe}}$  if the process is done irreversibly by placing the sample in liquid hydrogen at 13.96K?

$$\Delta S_{\text{sys}} \text{ (irreversible)} = \Delta S_{\text{sys}} \text{ (reversible)} = -110.4 JK^{-1}$$

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

$$\Delta H_{\text{sys}} = \Delta H_1 + \Delta H_2 = C_p \Delta T - \Delta_{\text{vap}} H = \frac{7}{2} R(T_2 - T_1) - \Delta_{\text{vap}} H$$

$$\Rightarrow \Delta H_{\text{sys}} = \frac{7}{2} (8.314)(90.19 - 293) - 6820 = -12.87 \times 10^3 J$$

$$\Delta S_{\text{surr}} = -\frac{(12.87 \times 10^3)}{90.19} = 922 JK^{-1}$$

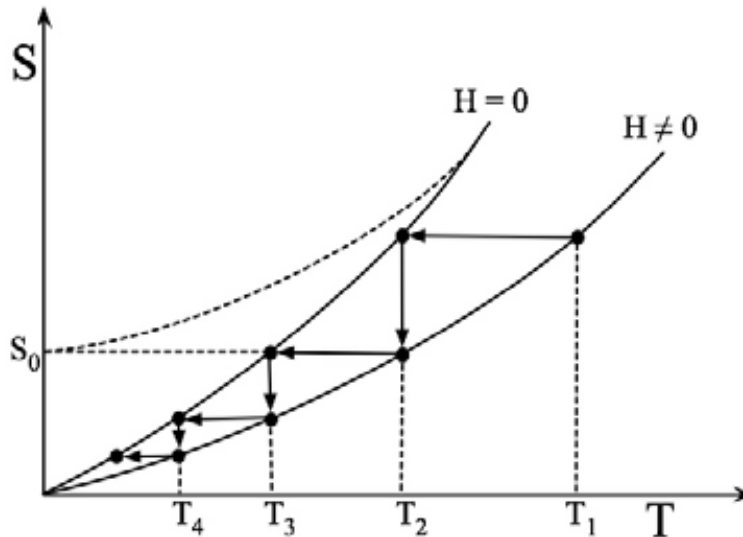
$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -110.4 + 922 = 812 JK^{-1}$$

4. (15%) Show that:  $\left(\frac{\partial p}{\partial T}\right)_E = -\frac{C_p - pV\alpha}{V(p\kappa - T\alpha)}$

$$\begin{aligned} \left(\frac{\partial p}{\partial T}\right)_E &= -\frac{\left(\frac{\partial E}{\partial T}\right)_p}{\left(\frac{\partial E}{\partial p}\right)_T} = -\frac{\left(\frac{\partial H}{\partial T}\right)_p - \left[\frac{\partial(pV)}{\partial T}\right]_p}{\left(\frac{\partial H}{\partial p}\right)_T - \left[\frac{\partial(pV)}{\partial p}\right]_T} = -\frac{C_p + p\left(\frac{\partial V}{\partial T}\right)_p}{-C_p\mu_{JT} - V - p\left(\frac{\partial V}{\partial p}\right)_T} \\ &= -\frac{C_p - pV\alpha}{-V(T\alpha - 1) - V + pV\kappa} = -\frac{C_p - pV\alpha}{V(p\kappa - T\alpha)} \end{aligned}$$

5. (15%) Describe the technique of adiabatic demagnetization **by a graph** and how this experiment can be linked to the third law of thermodynamics.

In 1926 Giauque and Debye independently showed that low temperature can be achieved by adiabatic demagnetization. In this technique a para- magnetic salt (gadolinium sulfate, for example) is repeatedly magnetized and then demagnetized. Demagnetization is accompanied by a decrease in temperature and it is found possible to reach 0.0014 K by the procedure.



- 1 Cooling by the Debye-Giauque adiabatic demagnetization method.

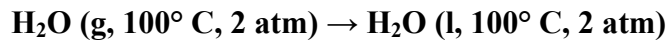
As a magnetic field  $H$  is turned on a paramagnetic salt, the entropy decreases from its value at  $H = 0$  because of the paramagnetic ordering effect of the magnetic field. Let us set

$$S_0 = \lim_{T \rightarrow 0} S(H = 0)$$

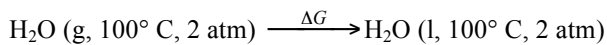
and assume that  $S_0 \neq 0$  contrary to the third law. Then it would be possible to attain  $T = 0$  in a single step of adiabatic demagnetization by starting the procedure at an appropriate temperature. This then would allow the system to reach  $T = 0$  in a finite number of steps. But since  $S_0 = 0$ , it is practically impossible to attain  $T = 0$  by a finite number of steps of adiabatic demagnetization since the temperature decrease achieved in each step gets smaller and smaller as the absolute zero is approached.

As a corollary to this theorem, we may state that *it is practically impossible to attain the unit efficiency for reversible Carnot cycles*. Since by

6. (20%) Water vapor can be maintained at 100°C and 2 atm pressure for a time, but it is in a state of metastable equilibrium and is said to be supersaturated. Such a system will undergo spontaneous condensation; the process is:

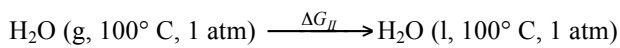


Calculate  $\Delta G_m$  for this process by devising suitable reversible paths. The molar enthalpy of vaporization  $\Delta_{\text{vap}}H_m$  is 40.60 kJ/mol; the density of water is 1.0 g/cm<sup>3</sup>; assume the vapor to behave ideally and liquid water is incompressible.



$\Delta G_I \downarrow$

$\uparrow \Delta G_{III}$



$$\Delta G = \Delta G_I + \Delta G_{II} + \Delta G_{III}$$

$$\Delta G_I = \int_{2\text{atm}}^{1\text{atm}} V_m dp \text{ at constant temp.} \Rightarrow \Delta G_I = \int_2^1 \frac{RT}{p} dp = RT \ln\left(\frac{1.0}{2.0}\right) = 8.314 \times 298 \times \ln \frac{1}{2}$$

$$= -1.72 \times 10^3 \text{ Jmol}^{-1}$$

$$\Delta G_{II} = 0 \text{ rev. phase transition}$$

$$\Delta G_{III} = \int_{1\text{atm}}^{2\text{atm}} V_m dp = V_m \int_1^2 dp \text{ if water is incompressible}$$

$$\Rightarrow \Delta G_{III} = V_m \Delta p = \left( \frac{1.0 \text{ cm}^3}{\text{g}} \times \frac{18 \text{ g}}{\text{mol}} \times \frac{10^{-6} \text{ m}^3}{\text{cm}^3} \right) \times (2-1) \text{ atm} \times \frac{10^5 \text{ Pa}}{\text{atm}} = 1.8 \text{ Jmol}$$

$$\therefore \Delta G = \Delta G_I + \Delta G_{II} + \Delta G_{III} \cong -1.72 \times 10^3 \text{ Jmol}^{-1}$$