

# NE 121 Fall 2005 Midterm Long Answer Solutions

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§ These solutions are for those who find Dr. Gilbert's solutions illegible or incomprehensible for some reason.

**Part 3:** Longer calculations: Please write as clearly as possible and show all your work. (15 points each).

1. How much does your car engine heat up when 2.500 g of octane  $C_8H_{18}$  (molar mass = 114 g/mol) is combusted to  $CO_{2(g)}$  and  $H_2O_{(g)}$  in an engine cylinder. Assume that the pressure inside your engine is atmospheric pressure and that no work is done. You forgot to put oil in the engine, so it seized and the pistons no longer move.

$$\Delta H_f^\circ C_8H_{18(l)} = -249.95 \text{ kJ/mol}$$

$$\Delta H_f^\circ CO_{2(g)} = -393.51 \text{ kJ/mol}$$

$$\Delta H_f^\circ H_2O_{2(g)} = -241.82 \text{ kJ/mol}$$

$$\Delta H_f^\circ O_{2(g)} = 0 \text{ kJ/mol}$$

Mass of car engine = 400 kg

Heat capacity of car engine = 0.200 J/g·K

## Solution

We have  $C_8H_{18(l)} + 12\frac{1}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(g)}$

$$\begin{aligned}\Delta H_f^\circ &= \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \\ &= 9(-241.82) + 8(-393.51) - (-249.95) \\ &= -2176.38 - 3148.08 + 249.95 \\ &= -5074.51 \text{ kJ/mol}\end{aligned}$$

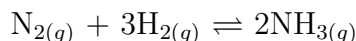
But 2.500 g of  $C_8H_{18}$  is  $(\frac{1 \text{ mol}}{114 \text{ g}}) = 0.0219 \text{ mol}$  of  $C_8H_{18}$ .

$$q = \Delta H/\text{mol} \times \text{no. of moles} = 5074.51 \frac{\text{kJ}}{\text{mol}} \times 0.0219 \text{ mol} = 111.28 \text{ kJ}$$

∴ For the car engine:

$$\begin{aligned}
 Q &= mC\Delta T \\
 \therefore \Delta T &= \frac{Q}{mC} \\
 &= \frac{111.28 \times 10^3 \text{ J}}{400 \times 10^3 \text{ g} \times 0.2 \frac{\text{J}}{\text{g}\cdot\text{K}}} \\
 &= \underline{\underline{1.39 \text{ K}}}
 \end{aligned}$$

2. At 25 °C for the synthesis of ammonia



$$K_p = 6.78 \times 10^5.$$

Calculate the equilibrium pressure of N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub> at 25 °C. The total pressure at equilibrium is 1.00 atm and the mole ratio of H to N at equilibrium is 3:1.

**Solution**

$$K_p = 6.78 \times 10^5 = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 \times P_{\text{N}_2}}$$

Also,

$$P_{\text{NH}_3} + P_{\text{H}_2} + P_{\text{N}_2} = 1 \text{ atm} \quad (1)$$

Since  $P_{\text{H}_2} = 3P_{\text{N}_2}$ , (1) becomes

$$P_{\text{NH}_3} + 4P_{\text{N}_2} = 1 \text{ atm}$$

Hence,

$$\frac{(1-4x^2)}{(3x^3) \times x} = K_p = 6.78 \times 10^5, \text{ where } x = P_{\text{N}_2}$$

In general, we cannot assume  $4x^2 \ll 1$  as this violates the 5% rule, but we will do it anyways to simplify the calculation.

$$K_p = 6.78 \times 10^5 = \frac{1^2}{27x^4}$$

$$\therefore x = P_{\text{N}_2} = \sqrt[4]{\frac{1}{27 \times 6.78 \times 10^5}} = \underline{\underline{1.53 \times 10^{-2} \text{ atm}}}$$

$$\text{and } P_{\text{H}_2} = 3x = 3 \times 1.53 \times 10^{-2} = \underline{\underline{4.59 \times 10^{-2} \text{ atm}}}$$

$$\text{Finally, } P_{\text{NH}_3} = 1 - 4x = (1 - 4 \times 1.53 \times 10^{-2}) = \underline{\underline{9.39 \times 10^{-2} \text{ atm}}}.$$

3. a. What is the pH of a 0.250 M solution of formic acid,  $K_a = 1.77 \times 10^{-4}$ ?

**Solution**

	$\text{HCOOH}_{(aq)}$	$+$	$\text{H}_2\text{O}_{(l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+_{(aq)}$	$+$	$\text{HCOO}^-_{(aq)}$
I	0.25		.		$\approx 0$		0
C	$-x$		.		$+x$		$+x$
E	$0.25 - x$		.		$x$		$x$

$$\text{So } K_a = 1.77 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{0.25-x}$$

Assume  $x \ll 0.25$ , or  $0.25 - x \approx 0.25$

$$\text{So } x = \sqrt{1.77 \times 10^{-4} \times 0.25} = 6.65 \times 10^{-3} \text{ M} = [\text{H}^+]$$

Assumption valid by 5% rule.

$$\therefore \text{pH} = -\log([\text{H}^+]) = -\log(6.65 \times 10^{-3}) = \underline{\underline{2.18}}$$

- b. You have no sodium formate in the lab to use to make a buffer. But you do have a stock solution of NaOH. What volume of a 10.0 M NaOH solution must you add to 1.00 L of the 0.250 M formic acid to make a buffer at pH of 4.00?

**Solution**

By the Henderson–Hasselback equation,

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{HCOO}^- + x]}{[\text{HCOOH} - x]}\right), \text{ if we add } x \text{ mol of OH}^-$$

$$4.00 = -\log(1.77 \times 10^{-4}) + \log\left(\frac{[\text{HCOO}^- + x]}{[\text{HCOOH} - x]}\right)$$

$$10^{0.248} = \frac{[\text{HCOO}^- + x]}{[\text{HCOOH} - x]}$$

$$1.25 = \frac{x}{0.25 - x}$$

$$0.4425 - 1.77x = x$$

$$\therefore x = \frac{0.4425}{2.77} = 0.1597 \text{ mol of OH}^-$$

$$\text{Volume of NaOH solution required} = \frac{\text{Moles of OH}^-}{[\text{OH}^-]} = \frac{0.1597 \text{ mol}}{10.0 \text{ M}} = \underline{\underline{1.60 \times 10^{-2} \text{ L}}}$$

4. 1.00 mol of an ideal gas at 298 K and 1 atm pressure is expanded isothermally and reversibly from 24.5 L to 245 L. It is then compressed isothermally and irreversibly back to initial conditions. Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  and  $\Delta S_{uni}$  for each step. Also Calculate  $\Delta S_{uni}$  for the cycle.

(a) **Reversible expansion**

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{-w}{T} = \frac{nRT \ln(\frac{V_2}{V_1})}{T} = 1 \times 8.31451 \times \ln(\frac{245}{24.5}) = 19.1 \text{ J/K}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = -\Delta S_{sys} = -19.1 \text{ J/K}$$

$$\Delta S_{uni_1} = \Delta S_{sys} + \Delta S_{surr} = 0 \text{ J/K}$$

(b) **Irreversible compression at constant P**

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{nRT \ln(\frac{V_f}{V_i})}{T} = 1 \times 8.31451 \times \ln(\frac{24.5}{245}) = -19.1 \text{ J/K}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-P\Delta V}{T} = \frac{-1 \text{ atm} \times (24.5 - 245) \text{ L}}{298 \text{ K}} \cdot \left( \frac{101.328 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = 75.0 \text{ J/K}$$

$$\Delta S_{uni_2} = \Delta S_{sys} + \Delta S_{surr} = -19.1 + 75.0 = +55.9 \text{ J/K}$$

(c) **Whole cycle**

$$\begin{aligned} \Delta S_{uni} \text{ for whole cycle} &= \Delta S_{uni_1} + \Delta S_{uni_2} \\ &= 0 \text{ J/K} + 55.9 \text{ J/K} \\ &= \underline{\underline{+55.9 \text{ J/K}}} \end{aligned}$$

The sign is positive as expected.

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