CHEM 1F92
FW2003/04

SOLUTIONS TO MIDTERM 2

Question 1. (6 marks)

Consider the reaction:

$$\text{rate}_{\text{rxn}} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = \frac{\Delta[P_4]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

$4\ PH_3\ (g) \rightarrow P_4\ (g) + 6H_2\ (g)$

In a certain experiment, 0.096 mol PH_3 (g) in a 2.0 L container is consumed in 20 seconds.

(Include UNITS in ALL of your answers; think CAREFULLY about signs.)

(a) What is $\Delta[PH_3]/\Delta t$? $-2.4 \times 10^{-3}\ M s^{-1}$

$$\frac{\Delta[PH_3]}{\Delta t} = \frac{[PH_3]_{final} - [PH_3]_{initial}}{t_{final} - t_{initial}} = \frac{-\frac{0.096\,mol}{2.0\,L}}{20\,s}$$

(b) What is the average rate of this reaction? $+6.0 \times 10^{-4}\ M s^{-1}$

$$\text{rate} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = -\frac{1}{4}(-2.4 \times 10^{-3}\,M s^{-1})$$

(c) What is $\Delta[P_4]/\Delta t$? $+6.0 \times 10^{-4}\ M s^{-1}$

$$\text{rate} = +\frac{\Delta[P_4]}{\Delta t}$$

(d) What is $\Delta[H_2]/\Delta t$? $+3.6 \times 10^{-3}\ M s^{-1}$

$$\text{rate} = +\frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

$$6.0 \times 10^{-4}\,\frac{M}{s} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

$$\frac{\Delta[H_2]}{\Delta t} = 6(6.0 \times 10^{-4}\,M s^{-1}) = 3.6 \times 10^{-4}\,M s^{-1}$$

Comments

$PH_3(g)$ is a reactant; it is consumed during reaction, therefore its concentration decreases with time.

$$\frac{\Delta[\text{reactants}]}{\Delta t} < 0$$

$$\frac{\Delta[\text{products}]}{\Delta t} > 0$$

Reaction rates are expressed as positive values and here

$$\text{reaction rate} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = \frac{\Delta[P_4]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

This is an "average" rate because it is measured over a range of time, i.e. 20 s.

$[\ ]$ means $\frac{mol}{L}$

$\therefore \frac{\Delta[\ ]}{\Delta t}$ means $\frac{mol}{L\,s}$ or $\frac{M}{s}$

Question 2. (2 marks)

The freezing point depression of an aqueous solution of a soluble salt was determined to be 7.44×10^{-2} °C. Which of the following solutions could this be? *(Assume ideal behaviour.)*

Circle the letter beside all correct answers:

[✓ (a)] 0.010 *m* Na_3PO_4 (aq) $Na_3PO_4(s) \rightarrow 3Na^+(aq) + PO_4^{3-}(aq)$

(b) 0.020 *m* $CaBr_2$ (aq) $CaBr_2(s) \rightarrow Ca^{2+}(aq) + 2Br^-(aq)$

(c) 0.040 *m* KCl (aq) $KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$

(d) 0.010 *m* $NaHCO_3$ (aq) $NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$

[✓ (e)] 0.020 *m* $CsClO_4$ (aq) $CsClO_4(s) \rightarrow Cs^+(aq) + ClO_4^-(aq)$

$$\underbrace{T_{fp}^{\circ} - T_{fp}} = K_f\, i m$$

$$7.44 \times 10^{-2}\,^{\circ}C = 1.86 \frac{^{\circ}C\,kg}{mol} \times i m$$

$$i m = 4.00 \times 10^{-2} \frac{mol}{kg} = 0.040\ m \text{ solute ion}$$

(a) $i = 4$ ions $i m = 4(0.010 m) = 0.040 m$ ✓

(b) $i = 3$ ions $i m = 3(0.020 m) = 0.060 m$ ✗

(c) $i = 2$ ions $i m = 2(0.040 m) = 0.080 m$ ✗

(d) $i = 2$ ions $i m = 2(0.010 m) = 0.020 m$ ✗

(e) $i = 2$ ions $i m = 2(0.020 m) = 0.040 m$ ✓

Comments on this question:

Most students who faired poorly did not know how to break a salt up into ions.

i is number of ions per unit formula

m is molality of salt solution

im is molality of solute ions in solution

Marking scheme:

+1 for each correct answer

mark subtracted for each additional wrong answer beyond the two correct answers

Question 3. (10 marks)

A coffee cup calorimeter can be used to measure the enthalpy of reaction when two solutions are mixed together (see Figure 6.7 from Chang, reproduced below):

2 mol HCl react per 1 mol $Ba(OH)_2$

$$2HCl\,(aq) + Ba(OH)_2\,(aq) \rightarrow BaCl_2\,(aq) + 2H_2O\,(l)$$

Consider 100.0 mL of 0.500 M HCl mixed together with 300.0 mL of 0.500 M $Ba(OH)_2$. The temperature of both solutions was initially 25.00°C and the final temperature was 26.76°C. Assume that the densities of all solutions are 1.00 g / mL and that all solutions have heat capacities equal to that of pure water.

(a) Is the above reaction endothermic or exothermic? exothermic

(b) How much solution, in grams, absorbs the heat of reaction? 400. g

(100.0 mL + 300.0 mL) × 1.00 g/mL

(c) What is the total heat change associated with this reaction? $+2.94 \times 10^3$ J or $-2{,}94\times1$

$q_{abs} = mC_p(T_f - T_i) = 400\,g \times 4.183 \frac{J}{K\,mol} (26.76°C - 25.0$

$q_{rxn} + q_{abs} = 0$

(d) How many moles of HCl reacted? 5.00×10^{-2} mol

$0.100\,L \times 0.500 \frac{mol}{L} = 5.00 \times 10^{-2}\,mol$

(e) How many moles of $Ba(OH)_2$ reacted? $5.00 \times 10^{-2}\,mol\,HCl \times \frac{1\,mol\,Ba(OH)}{2\,mol\,HCl}$

HCl is limiting reagent! $= 2{,}50 \times 10^{-2}\,mol$

(f) What is ΔH°_{rxn} for 2 moles of HCl (aq) reacting with 1 mole of $Ba(OH)_2$ (aq)? *(Hint: use your answer in part (c); Show your work!)*

$\Delta H^\circ_{rxn} = q_{rxn}$ $\quad q_{rxn} = \frac{-2.94 \times 10^3\,J}{5.00 \times 10^{-2}\,mol\,HCl}$

$\Delta H^\circ_{rxn} = \frac{-2{,}94 \times 10^3\,J}{5.00 \times 10^{-2}\,mol\,HCl} \times 2\,mol\,HCl = -118\,kJ$

(g) **Circle** the number beside the best name for the type of reaction above:
- (1) precipitation
- (2) combustion
- (3) oxidation-reduction
- [✓ (4)] neutralization
- (5) hydration

acid + base → water

HCl $\quad Ba(OH)_2$

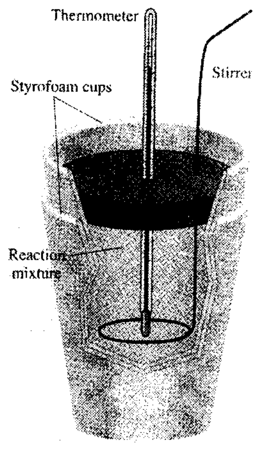


FIGURE 6.7 *A constant-pressure calorimeter made of two Styrofoam coffee cups. The outer cup helps to insulate the reacting mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed by the reaction can be determined by measuring the temperature change.*

From: Chang, Chemistry 7th Edition, McGraw-Hill, 2002.

Comments on this question:

When you see a problem broken into pieces like this, I am trying to guide you towards the correct answer.

a) Why did the temperature increase? Because the reaction
$2HCl(aq) + Ba(OH)_2 \rightarrow BaCl_2(aq) + 2H_2O(l)$
gave off heat!
It is exothermic.

b) The solution is an aqueous (water) mixture. The mass of a liquid solution is given by volume × density.
Total volume = 100.0 mL HCl(aq) + 300.0 mL $Ba(OH)_2$ = 400.0 mL

$$\text{mass solution} = 400.0\,\text{mL} \times \frac{1.00\,\text{g}}{\text{mL}}$$

c) This asked for <u>heat</u> change not temperature change!

heat ≡ q

Heat absorbed by solution

$$q_{abs} = \underset{\substack{\swarrow \\ \text{400. g} \\ \text{from part B}}}{m}\,\underset{\substack{\searrow \\ \text{heat capacity of} \\ \text{water}}}{\bar{C}_p}\,(T_f - T_i)$$

$$q_{rxn} + q_{abs} = 0$$

$$\left.\begin{aligned} q_{abs} &= +2.94 \times 10^3\,\text{J} \\ q_{rxn} &= -2.94 \times 10^3\,\text{J} \end{aligned}\right\}$$

we accepted either although I asked for q_{rxn}.

d) moles HCl in 100.0 mL 0.500 M HCl

$$= 0.1000\ L \times 0.500\ \frac{mol}{L}$$

$$= 5.00 \times 10^{-2}\ mol$$

e) moles $Ba(OH)_2$ in 300.0 mL 0.500 M

$$= 0.3000\ L \times 0.500\ \frac{mol}{L}$$

$$= 15.0 \times 10^{-2}\ mol$$

Now, 2 moles HCl react with 1 mole $Ba(OH$

∴ $Ba(OH)_2$ is in excess!

Moles $Ba(OH)_2$ that reacted with HCl

$$= 5.00 \times 10^{-2}\ mol \times \frac{1\ mol\ Ba(OH)_2}{2\ mol\ HCl}$$

$$= 2.5 \times 10^{-2}\ mol$$

f) $\Delta H^\circ_{rxn} = q_{rxn}$

from part(c)!

$= -\frac{2.94 \times 10^{3}\,J}{5.00 \times 10^{-2}\,mol\,HCl} \times 2\,mol\,HCl$

from part (d)!

$= -118\,kJ$

Part (a) was supposed to get you thinking about this sign!

g) $2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$

No solids seen on product side
∴ cannot be precipitation

Not combustion, which is burning a compound in $O_2(g)$ to produce $CO_2(g)$ and $H_2O(l)$. Rather hard to accomplish in aqueous solution!

$HCl \rightarrow$ acid
$Ba(OH)_2 \rightarrow$ base

neutralization!
acid + base → water

Question 4. (10 marks)

(1 part mark total awarded for (a) plus (b) ONLY if zero marks obtained for (c) – (g)!)

(a) Calculate the molar mass of pentane: 72.15 g/mol

(b) Calculate the molar mass of hexane: 86.18 g/mol

A solution is prepared by mixing 25.0 mL liquid pentane (C_5H_{12}; density = 0.626 g/cm^3) with 45.0 mL liquid hexane (C_6H_{14}; density = 0.660 g/cm^3). Assume that the volume of the final solution is the sum of the volumes of pentane and hexane.

Compute the following for the above solution of pentane in hexane:

(c) Mass % pentane 34.5%

(d) Mole fraction pentane 0.386

(e) Molality of pentane 7.30 mol/kg

(f) Molarity of pentane 3.10 mol/L

(g) Density of the pentane/hexane solution

$$\frac{15.65\text{g pentane} + 29.70\text{g hexane}}{25.0\text{mL pentane} + 45.0\text{mL hexane}} = 0.648\text{ g/mL}$$

$$\text{(a)}\quad 25.0\text{mL} \times 0.626\frac{\text{g}}{\text{mL}} = 15.65\text{g pentane} \quad (0.2169\text{ mol})$$

$$45.0\text{mL} \times 0.660\frac{\text{g}}{\text{mL}} = 29.70\text{g hexane} \quad (0.3446\text{ mol})$$

$$\text{mass \% pentane} = \frac{15.65\text{g pentane}}{15.65\text{g pentane} + 29.70\text{g hexane}} \times 100\%$$

$$\text{b) mole fraction pentane} = \frac{0.2169\text{ mole pentane}}{0.2169\text{ mole pentane} + 0.3446\text{ mole hexane}}$$

$$\text{c) molality of pentane} = \frac{0.2169\text{ mole pentane}}{0.02970\text{ kg hexane}}$$

$$\text{d) molarity of pentane} = \frac{0.2169\text{ mole pentane}}{0.0250\text{ L} + 0.0450\text{ L}}$$

Comments on this question:

$$1\ \mathrm{mL} \equiv 1\ \mathrm{cm}^3$$

Question 5. (10 marks)

Nitroglycerin, $C_3H_5(NO_3)_3$, is an explosive compound that decomposes according to:

$$4\ C_3H_5(NO_3)_3\ (s) \rightarrow 12\ CO_2\ (g) + 10\ H_2O\ (g) + 6\ N_2\ (g) + O_2\ (g)$$

The molecular weight of nitroglycerin is 227.083 g/mol.

(a) What is the mole fraction of N_2 (g) in the mixture of product gases?

0.207 or 6/29

$$\frac{6 \text{ mol } N_2}{12 \text{ mol } CO_2 + 10 \text{ mol } H_2O + 6 \text{ mol } N_2 + 1 \text{ mol } O_2} = \frac{6}{29}$$

(b) What is the partial pressure of N_2 (g) in the mixture of product gases if the total pressure is 1.20 atm? 0.248 atm

$$P_{N_2} = X_{N_2} P_T = \frac{6}{29} \times 1.20 \text{ atm} = 0.248 \text{ atm}$$

(c) **Calculate** the total volume of gas collected at 1.20 atm and 25°C from the complete decomposition of 2.60×10^2 g of nitroglycerin. *(Show your work!)*

$$\text{moles } C_3H_5(NO_3)_3(s) = \frac{2.60 \times 10^2 \text{ g}}{227.083 \text{ g/mol}} = 1.145 \text{ mol}$$

$$4\ C_3H_5(NO_3)_3(s) \longrightarrow 12\ CO_2(g) + 10 H_2O(g) + 6 N_2(g) + O_2(g)$$

$$\text{moles product gas} = \frac{29 \text{ moles gas products}}{4 \text{ moles } C_3H_5(NO_3)_3} \times 1.145 \text{ mol } C_3H_5(NO_3)$$

$$= 8.301 \text{ moles product gases}$$

$$PV = nRT$$

$$V = \frac{8.301 \text{ mol} \times 0.08201 \frac{\text{L atm}}{\text{K mol}} \times 298 \text{ K}}{1.20 \text{ atm}}$$

$$V = 169 \text{ L}$$

Question 5. (*continued …*)

$$4\ C_3H_5(NO_3)_3\ (s) \rightarrow 12\ CO_2\ (g) + 10\ H_2O\ (g) + 6\ N_2\ (g) + O_2\ (g)$$

(d) The heat of formation of nitroglycerin is 136.5 kJ/mol.
Compute ΔH°_{rxn} for the decomposition of exactly 4 moles of nitroglycerin:
(Show your work! Thermodynamic values are at end of the exam paper ….)

$$\Delta H^\circ_{rxn} = \sum \underset{\underset{CO_2,\ H_2O(g),\ N_2,\ O_2}{\downarrow}}{n\Delta H^\circ_f\ (\text{products})} - \sum \underset{\underset{C_3H_5(NO_3)_3}{\downarrow}}{m\Delta H^\circ_f\ (\text{reactants})}$$

$$\Delta H^\circ_{rxn} = 12\ \cancel{\text{moles}}\left(-393.509\ \frac{kJ}{\cancel{mol}}\right) + 10\ \cancel{\text{moles}}\left(-241.818\ \frac{kJ}{\cancel{mol}}\right)$$

$$+\ 6\ \cancel{\text{moles}}\left(0\ \frac{kJ}{mol}\right) + 1\ \cancel{mol}\left(0\ \frac{kJ}{\cancel{mol}}\right)$$

$$-\ 4\ \cancel{\text{moles}}\left(136.5\ \frac{kJ}{mol}\right)$$

$$\Delta H^\circ_{rxn} = -7686.3\ kJ$$

Comments on this question:

$X_{N_2} = \frac{6}{29}$ these are exact numbers, therefore as many sig figs as you need.

I accepted 2 or more sig figs but one s.f. was not enough.

$P_{N_2} = 0.248$ atm 3 sf dictated by 1.20 atm total pressure

Partial pressure < Total pressure!

The nitroglycerin decomposes into $12\, CO_2(g) + 10\, H_2O(g) + 6 N_2(g) + O_2(g)$. You must take moles of these gases into consideration when calculating the volume!

Sig figs in ΔH°_{rxn} determined by addition and subtraction rules. Therefore properly 1 dp (−7686.3 kJ). I did accept (−7686 kJ) however.

Question 6. (12 marks)

The following is a table containing vapour pressures for various liquids at 20°C:

Compound	Benzene	Acetic acid	Acetone	Diethyl ether	Water
Molecular Formula	C_6H_6	CH_3COOH	CH_3COCH_3	$CH_3CH_2OCH_2CH_3$	H_2O
Vapour Pressure at 20°C	80 torr	11.7 torr	184.8 torr	442.2 torr	17.5 torr

(a) Which compound is likely to have the **lowest** boiling point? diethyl ether
has the highest vp ∴ will boil at lowest T

(b)

(i) Which compound has the **strongest** intermolecular interactions? aceticacid or H_2O

(ii) What is the **name** of this intermolecular interaction? hydrogen bonding or dipole-dipole

(c) Propane has the following vapour pressures:

	Temperature (°C)	Vapour Pressure (torr)
180.75 K	-92.4	40
225.85 K	-47.3	600

Compute ΔH_{vap} for propane. *(Report your answer to 3 sig. figs; show your work!!!)*

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{vap}}{R} \left\{ \frac{T_1 - T_2}{T_1 T_2} \right\}$$

$$\ln \frac{40}{600} = \frac{\Delta H_{vap}}{8.314 \frac{J}{K\,mol}} \left\{ \frac{180.75\,K - 225.85\,K}{(180.75\,K)(225.85\,K)} \right\}$$

$$-2.708 = \Delta H_{vap} \times -1.329 \times 10^{-4} \frac{1\,mol}{J}$$

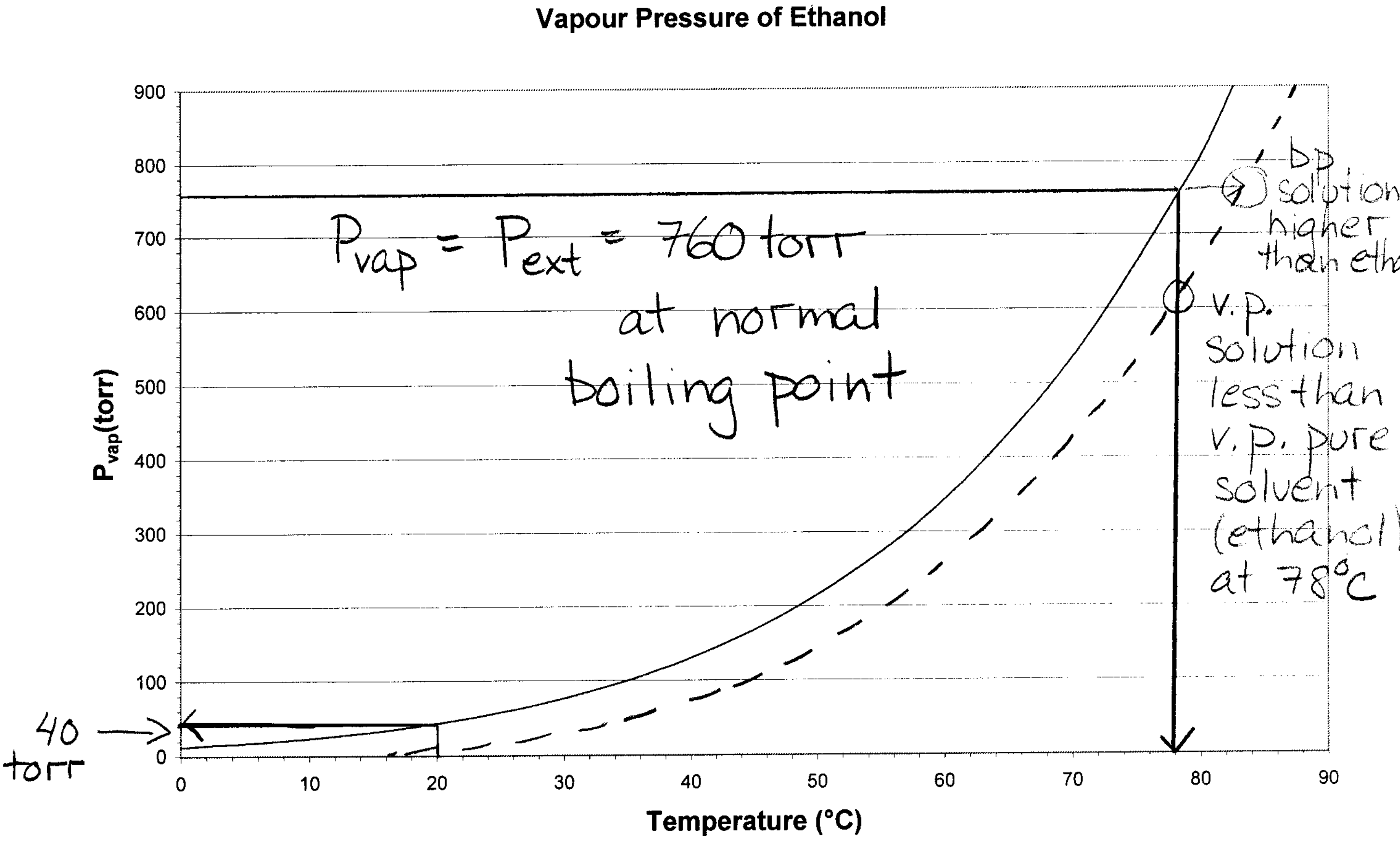
$$\Delta H_{vap} = 2.04 \times 10^{4}\ J/mol$$

or

20.4 kJ/mol

Question 6. (*continued …*)

(d) Using the diagram below, what is the vapour pressure of ethanol at 20°C? 40 torr



(e) Using the diagram above, what is the value of the normal boiling point of ethanol? 78°C

(f) A small amount of glucose is dissolved in a sample of ethanol. **Circle** the correct symbol below (T_{bp} is the boiling point):

T_{bp} (glucose-ethanol solution) [✓ >] = < T_{bp} (ethanol)

boiling point elevation

2 MARK BONUS:

(g) On the diagram above, **sketch** what you think the vapour-pressure-temperature curve looks like for the glucose-ethanol solution.

see above.

vapour pressure of solution < vp pure solvent at given T