Part 1. Short Answer [2 marks each]

1. What are three ways we have of predicting whether a reaction will be spontaneous or not?

   -1 for any missed

   Spontaneous means $\Delta G < 0$, $\Delta S_{univ} > 0$, $K > 1$

2. What is the standard state for ions in aqueous solution?

   1 Molar concentration (2)

3. Define enthalpy of formation.

   $\Delta_f H$ = ΔH of the reaction (1) forming a compound from its constituent elements in their standard states (1)

4. For each pair listed below, select which has the greater entropy.

   $H_2O(l)$ vs $H_2O(g)$

   $O_2(g)$ at 298 K vs $O_2(g)$ at 400 K

   butane vs cyclo-butane

   NaCl (s) vs NaCl (aq)

   .5 each

5. Define a Bronsted base.

   A Bronsted Base is a proton acceptor

6. For the following reactions, identify the acid and its conjugate base.

   $CH_3COOH(aq) + H_2O(l) \rightarrow H_3O^+(aq) + CH_3COO^-$

   acid (1) (CH_3COOH); conj. base (1) (CH_3COO^-)

Part 2.

1: The reaction I_2 (g) ⇌ 2I (g) was studied by sealing solid iodine, I_2, in a glass bulb and measuring the total equilibrium pressure in the bulb at various temperatures (the I_2 completely sublimes). The following data was obtained:

Volume of the bulb = 249.8 ml; original mass of I_2 = 0.497 g; MW(I) = 127 g/mol

T(°C)	Total Equilibrium Pressure (atm)
800	0.734
1000	0.984

(a) show that the equilibrium pressure of I_2 (g) is $2P_o - P_t$ and that of I (g) is $2(P_t - P_o)$, where P_o is the original pressure of I_2 (g) (at the particular temperature in question, when no decomposition occurs) and P_t is the total pressure in the bulb at equilibrium. Assume ideal gas behaviour throughout. [3]

(b) Calculate K_p for each temperature. [2]

(c) Calculate ΔH° for the reaction in the temperature range 800°C to 1000°C (assume ΔH° is independent of temperature). [3]

(d) Calculate the free energy and entropy change for the reaction at 800°C. [4]

(a) $I_2 \rightleftharpoons 2I$

P_0 0

$P_0 - x$ $+2x$

$P_0 - x$ $2x$ $P_T = P_0 - x + 2x = P_0 + x$

$x = P_T - P_0$

Equil (I_2) $P_0 - (P_T - P_0) = 2P_0 - P_T$

(I) $2(P_T - P_0)$

(b) $K = \frac{[2(P_T - P_0)]^2}{2P_0 - P_T}$

$P_0 = \frac{nRT}{V}$ at each T

$n = \frac{0.497g}{2(127 g/mol)} = 1.96 \times 10^{-3}$ moles

$P_0 (800°C) = \frac{1.96 \times 10^{-3} mol (R)(1073K)}{0.2498 L}$

$= 0.69$ atm.

$P_0 (1000°C) = 0.82$ atm.

$K_{800} = 1.20 \times 10^{-2}$

$K_{1000} = 1.64 \times 10^{-1}$

c) $\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\Delta H^\circ = 148$ kJ/mol.

d) at 1073K. $\Delta G^\circ = -RT \ln K$

$= 39.5$ kJ/mol

$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$

$= 101$ J/K mol

2: The standard enthalpies of combustion of 1,2-butadiene ($C_4H_6(g)$), butane ($C_4H_{10}(g)$) and $H_2(g)$ are -2540.2 kJ/mol, -2877.6 kJ/mol and -285.8 kJ/mol, respectively (in each case $CO_2(g)$ and $H_2O(l)$ are formed). Use this data to calculate the enthalpy of hydrogenation of butadiene, for which the unbalanced equation is: [12 marks]

$C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10}(g)$ balance

combustion.

(1) $C_4H_6 + \frac{11}{2}O_2 \rightarrow 4CO_2 + 3H_2O_l$ $\Delta H = -2540.2$ kJ/mol

(2) $C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O_l$ $\Delta H = -2877.6$

(3) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O_l$ ΔH -285.8 kJ

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(1) $C_4H_6 + \frac{11}{2}O_2 \rightarrow 4CO_2 + 3H_2O$ -2540.2

$-$(2) $4CO_2 + 5H_2O_l \rightarrow C_4H_{10} + \frac{13}{2}O_2$ $+2877.6$

$2\times$(3) $2H_2 + O_2 \rightarrow 2H_2O_l$ $2(-285.8)$

$C_4H_6 + 2H_2 \rightarrow C_4H_{10}$ -234.2 kJ/mol

3. What must be the molarity of an aqueous solution of trimethylamine ($(CH_3)_3N$) if it has a pH = 11.12? (Hint, you will need to do your ICE table backwards!). [8 marks]

$(CH_3)_3N(aq) + H_2O(l) \rightarrow OH^-(aq) + (CH_3)_3NH^+(aq)$ $K_b = 6.3 \times 10^{-5}$ M

pH = 11.12 pOH = 14 − 11.12 = 2.88

$[OH^-] = 0.0013$ M.

$$K_b = \frac{[OH^-][(CH_3)_3NH^+]}{[(CH_3)_3N]} = 6.3\times10^{-5} M$$

	$(CH_3)_3N$	OH^-	$(CH_3)_3NH$
I	x	0	0
C	x − 0.0013	0.0013	0.0013
E	0.027M	0.0013	0.0013

at equil. $[OH^-] = [(CH_3)_3NH^+]$

$$K_b = \frac{(0.0013M)^2}{[(CH_3)_3N]_{eq}}$$

$[(CH_3)_3N]_{eq} = 0.027$ M.

∴ x = 0.027 + 0.0013 = **0.028 M**

4. For 0.045 M H_2CO_3, a weak diprotic acid, calculate (a) $[H_3O^+]$, (b) $[HCO_3^-]$ and (c) $[CO_3^{2-}]$.
[14 marks]
$K_{a1} = 4.4\times10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$

start with 1st dissociation

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

	H_2CO_3	H_3O^+	HCO_3^-
i	0.045M	0	0
c	$-x$	x	x
e	$0.045-x$	x	x

$$K = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.045-x} = 4.4\times10^{-7} M$$

solving. either by assumption or quadratic eq. -
$x = 1.4\times10^{-4} M$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

	HCO_3^-	H_3O^+	CO_3^{2-}
	1.4×10^{-4}	1.4×10^{-4}	0
c	$-x$	$+x$	x
e	$1.4\times10^{-4}-x$	$1.4\times10^{-4}+x$	x

$$K = \frac{(1.4\times10^{-4}+x)(x)}{1.4\times10^{-4}-x} = 4.7\times10^{-11}$$

solving $x = 4.7\times10^{-11}$ ⇐ you may also get "0"

so, $[H_3O^+] = 1.4\times10^{-4} M$, $[HCO_3^-] = 1.4\times10^{-4} M$

$[CO_3^{2-}] = 4.7\times10^{-11} M$.
↑ also "0"