Thermodynamics past exam questions with answers

Practical Physical And Applied Chemistryand Chemical Analysis (University of Strathclyde)

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13.253 – Thermodynamics
Past Exam Questions with answer outlines

Warning! Read and think about this paragraph before looking further. You are strongly encouraged NOT to look at these answer notes until you have tried some past paper questions for yourself. There are worked examples of all types covered by this class in the extended lecture notes given out earlier. Although looking at worked examples is usually helpful in learning how to do calculations, it is almost never enough by itself. Most of us go through 3 stages in dealing with a particular type of problem. At first it all seems totally obscure. But after some study, it becomes possible to look through a worked example and understand what is happening at each step. However, trying to do a problem for yourself without looking at the worked example may still get nowhere. But it is only by trying problems like this, and eventually succeeding, that you reach the final stage where you can tackle any problem unseen. (Usually by now everything seems so easy!). So be very careful about looking at these worked solutions before attempting the questions – these problems are a chance to practice unseen calculations for yourself. You can of course also get help and advice if you attempt these problems and get stuck – particularly during the tutorial sessions.

Even if you can't resist the temptation to look at the worked answers before attempting the problems, I would strongly encourage you to make your own attempt later. Put away the worked examples, wait a few days, then try the exam problems for yourself without looking at worked answers.

Beware also of one other danger with worked examples. For most calculations there are several logical ways to do them, for example changing the order in which steps are done. So do not necessarily worry if your working looks very different from the worked examples – it may well be almost right, even if you don't have the correct answer. This is where advice from a tutor is so useful – to identify exactly where you have gone wrong. It's quite rare to find that someone has approached the problem in completely the wrong way – usually it's just a relatively small slip in basically a correct method. Surprisingly often the problem is in arithmetic or calculator use – if you don't get the right answer, it's always a good idea to check your arithmetic before anything else.

Jan 2013, Q1

a) Why can we never give a value of enthalpy or internal energy for a chemical system (e.g. a compound in its standard state)? What is different that allows us to give a value of entropy for such a system? [4]

b) Outline how you could calculate the entropy of a gas in its standard state, explaining what experimental data would be needed. [4]

c) Explain what values we can use for the thermodynamic activities of:

i. A pure crystalline solid
ii. A pure liquid

iii. One compound in a gaseous mixture
iv. A compound in dilute solution [5]

d) For the reaction:
$HgO\ (s) + SO_2\ (g)$ ==== $Hg\ (l) + SO_3\ (g)$
$\Delta_r G^o = -13.6$ kJ mol^{-1} at 120 ºC. Calculate $\Delta_r G$ when the partial pressures are 0.1 bar for SO_3 and 0.004 bar for SO_2. [6]

e) Calculate the equilibrium constant for the reaction, and hence state what will be the mole fraction of SO_3 in the gas phase at equilibrium. [6]

Answer notes:

a) Experimentally we can only measure changes in enthalpy and internal energy (and indeed in entropy). For H and U there is no sensible way to define a zero level, so we can only ever present changes, such as $\Delta_f H$ values, based on defining them to be zero for elements in their standard states. For entropy, the Third Law allows us to define entropy as zero for any perfect crystalline substance at 0 K. By then measuring entropy changes during heating to temperatures of interest, we can give an absolute value of entropy.

b) You need to measure the heat capacity as a function of temperature, essentially all the way up from 0 K, and the enthalpies of fusion and vapourisation. Then integrate Cp.dT/T all the way from 0 K, adding in ΔH/T at each phase change temperature.

c)
i. This can be set as 1 by definition
ii. The activity of a pure liquid is also set at 1 by definition
iii. At pressures where the ideal gas law holds well, we can take the partial pressure in bar as a very good approximation to the thermodynamic activity
iv. In sufficiently dilute solution the activity of any solute can be set equal to its molar concentration. At higher concentrations, the concentration is multiplied by an activity coefficient which is slightly different from 1 (usually < 1).

d) $\Delta_r G = \Delta_r G^o + RT\ln Q$
For this reaction

$$Q = \frac{a_{Hg} a_{SO_3}}{a_{HgO} a_{SO_2}} = \frac{1.p_{SO_3}}{1.p_{SO_2}} = \frac{0.1}{0.004} = 25$$

$\Delta_r G = -13600$ J mol^{-1} + 8.314 J mol^{-1}K^{-1} × 393 K × ln(25)
= -13600 J mol^{-1} + 10500 J mol^{-1} = -3100 J mol^{-1} = -3.1 kJ mol^{-1}

e) $\Delta_r G^o = -R.T.\ln K$

$$\ln K = \frac{-\Delta_r G^o}{R.T} = \frac{13600 Jmol^{-1}}{8.314 Jmol^{-1}K^{-1} \times 393K} = 4.16$$

K = 64.2

So at equilibrium the partial pressure of SO_3 will be 64 times that of SO_2. Let x be the mole fraction of SO_3, so x/(1-x) = 64, x = 64 – 64x, 65x = 64, x = 64/65 = 0.985.

Jan 2013, Q2

a) Explain how experiments in electrochemical cells can approach the limit of thermodynamic reversibility. Why can practical rechargeable batteries not be operated in a thermodynamically reversible manner? [6]

b) Write out the half cell reaction for the redox couple SO_4^{2-}/ SO_3^{2-} under alkaline aqueous conditions. [2]

c) Write out the reaction equation for a complete electrochemical cell whose potential would be the standard electrode potential of this couple. Also write out how this cell would be shown in cell notation [3]

d) This standard electrode potential for SO_4^{2-}/ SO_3^{2-} under alkaline aqueous conditions is equal to -0.93 V. We also have:

$$2\ H_2O + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-(aq) \quad E^o = -0.828\ V.$$

Write out the cell reaction equation for the reduction of sulfate by H_2 under alkaline aqueous conditions and calculate E^o_{cell}. [5]

e) Hence calculate $\Delta_r G^o$ for sulfate reduction by H_2 in alkali, and comment on whether this reaction will be thermodynamically favourable. [6]

f) Explain why the E^o_{cell} values are different for the reactions written in parts (c) and (d), and comment on the relationship between them. [3]

Answer notes:-

a) Expect idea that an electrochemical cell at balance (zero current) is at the thermodynamically reversible limit – by allowing a minute current we can stay close to reversibility, potentially cycling between current generation and electrolysis. The smaller the current the closer we approach, but can never quite get there – this would require infinitely slow change with zero current. Practical rechargeable batteries have to charge and discharge at useful rates, so cannot be very close to the limit – the cyclic process generates entropy, not all the electrical energy is recovered, some is converted to heat.

b) $SO_4^{2-}\ (aq) + H_2O + 2\ e^- === SO_3^{2-}\ (aq) + 2\ OH^-\ (aq)$

c) SO_4^{2-} (aq) + H_2O + H_2 (g) === SO_3^{2-} (aq) + 2 OH^- (aq) + 2 H^+ (aq)
(not correct to re-combine the OH^- and H^+, they are in separate half cells!)
Pt|H_2 (1 bar)|H^+ (aq), a= 1|| SO_4^{2-} (aq), SO_3^{2-} (aq), OH^- (aq), all a = 1|Pt

d) SO_4^{2-} (aq) + H_2 (g) === SO_3^{2-} (aq) + H_2O
E^o_{cell} = E^o (cathode) - E^o (anode)
= -0.93 - -0.828 V = - 0.10 V

e) $\Delta_r G^o = -n.F.E^o_{cell}$
$= -2 \times 96480\ J\ V^{-1} mol^{-1} \times -0.10\ V = +19300\ J\ mol^{-1} = +19.3\ kJ\ mol^{-1}$
This is thermodynamically unfavourable under standard conditions, but the absolute value is sufficiently small that the reaction may proceed under some conditions.

f) Essentially because these are different cell reactions, so they will have different E^o_{cell} values. The difference between the reactions is the ionisation of 2 molecules of water. The difference in the two $\Delta_r G^o$ values would be a measure of the Gibbs energy of water ionisation.

August 2013, Q1

a) It is possible to construct an electrochemical cell such that E_{cell} will be the standard electrode potential of the Fe^{2+}/Fe couple. Write out this cell in cell notation, write the equation for the cell reaction, and draw a diagram showing the key features of the cell. [8]

The following cell at 25 °C is being used:
Cu|Cu^{2+} (aq, 0.01 M) || Cu^{2+} (aq, a = 1))|Cu E_{cell} = +0.077 V

b) Write out the cell reaction. Explain why E_{cell} is not zero. [3]

c) Calculate the activity of 0.01 M Cu^{2+} in the left hand electrolyte solution. [6]

d) In the left hand half cell electrolyte, the macrocyclic polyether 18-crown-6 has also been added at a total concentration of 10^{-5} M. This compound is able to form a complex with Cu^{2+} ions according to:
Cu^{2+} + 18-crown-6 ==== Cu^{2+}.crown
In this electrolyte solution, 46% of the 18-crown-6 is found to be present as the complex with Cu^{2+}. Estimate the activity-based equilibrium constant for the complexation, stating any assumptions or approximations you need to make. [8]

Outline answer

a) Pt|H_2 (g, 1 bar)|H^+ (aq, a = 1)||Fe^{2+} (aq, a=1)|Fe
H_2 (g) + Fe^{2+} (aq) → 2 H^+ (aq) + Fe (s)
The diagram should show: one half cell with aqueous H^+ solution, a Pt electrode, and H_2 gas bubbled over it; the second half cell with Fe^{2+} in solution and an Fe electrode; an electrical connection between the electrodes via a voltmeter; a salt bridge connecting the electrolytes.

b) Cu (s) + Cu^{2+} (aq, a = 1) → Cu (s) + Cu^{2+} (aq, 0.01 M), or just
Cu^{2+} (aq, a = 1) → Cu^{2+} (aq, 0.01 M)
Although there is no change in the chemical species present, Cu^{2+} is being removed from a more concentrated (higher activity) solution and added to a relatively dilute (lower activity) one. This spontaneous process has a non-zero (in fact negative) Gibbs energy change, and hence a non-zero, positive E_{cell}.

c) $E_{cell} = E^o_{cell} - (RT/nF)\ln Q$
In this case $E^o_{cell} = 0$, because both redox couples are the same; and n = 2, the number of electrons transferred in the cell reaction as written above.
Hence

$$\ln Q = -\frac{nFE_{cell}}{RT} = -\frac{2 \times 9.648 \times 10^4\, JV^{-1}mol^{-1} \times 0.077V}{8.314 Jmol^{-1}K^{-1} \times 298K} = -6.00$$

$$Q = 0.00248 = \frac{a_{Cu^{2+}}(0.01M)}{a_{Cu^{2+}}(a = 1)} = a_{Cu^{2+}}(0.01M)$$

d) For the reaction: Cu^{2+} + 18-crown-6 ==== Cu^{2+}.crown

We have the activity of Cu^{2+} from part (c). Both the free crown ether and the complex are present at very low concentrations, so we take their activity coefficients as close to 1. Hence their activity ratio will be almost the same as their concentration ratio. Thus we get

$$K = \frac{a_{Cu.^{2+}crown}}{a_{Cu^{2+}}.a_{crown}} = \frac{1}{a_{Cu^{2+}}}.\frac{[Cu^{2+}.crown]}{[crown]} = \frac{1}{0.00248}.\frac{46}{54} = 342$$

August 2013, Q2

a) Explain why the change in internal energy and in enthalpy may not be equal for a reaction done at constant pressure, and how the difference between them may be estimated. Explain why measurements in a bomb calorimeter give Δ_rU, not Δ_rH. [9]

b) When 120 mg of naphthalene ($C_{10}H_8$(s)) was burned in a bomb calorimeter the temperature rose from 25 °C by 3.05 K. The following Δ_fH^o (298 K) values, all in kJ mol^{-1} are known: $C_{10}H_8$(s), +78.5; CO_2 (g), -393.5; and H_2O (l) -285.8. Calculate the calorimeter constant (amount of heat to raise temperature by 1 K). [7]

c) When 100 mg of phenol ($C_6H_5OH(s)$) is burned under the same conditions the rise in temperature is 2.05 K. Calculate the value of $\Delta_f H^o$ (298 K) for phenol. [9]

Outline answer:

a) Change in enthalpy is heat transferred at constant pressure. But change in internal energy also includes work done on or by the system. If the volume changes as a result of a reaction at constant pressure, work will be done, so $\Delta_r U$ will differ from $\Delta_r H$ by the amount of this work. In condensed phases (solids and liquids) the work is insignificant, but if gases are involved, it is significant, although usually still a fairly small correction. The work is given by $p\Delta V$. For gases we can write $V = nRT/p$, or at constant T and p, $\Delta V = \Delta nRT/p$, where Δn is the change in number of moles of gas as a result of the reaction. Hence the work, $p\Delta V = \Delta nRT$, and so we get $\Delta_r U = \Delta_r H - \Delta_r nRT$ (If $\Delta_r n$ is positive, the system does work, so $\Delta_r U$ is slightly smaller than $\Delta_r H$. The bomb calorimeter is designed to work at constant volume, so no work is done. Hence the heat evolved tells us $\Delta_r U$, and we have to correct using the above equation to get $\Delta_r H$.

b) $C_{10}H_8(s) + 12\ O_2\ (g) \rightarrow 10\ CO_2\ (g) + 4\ H_2O\ (l)$

$\Delta_r H^o$ = Sum for products of ($\nu \times \Delta_f H^o$) - Sum for reactants of ($\nu \times \Delta_f H^o$)

$= (10 \times -393.5) + (4 \times -285.8) - (1 \times 78.5 + 12 \times 0) = -5156.7$ kJ mol^{-1}

But because the reaction is carried out at constant volume, we want

$\Delta_r U^o = \Delta_r H^o - \Delta_r nRT = -5156700$ J mol^{-1} $- (10-12) \times 8.314$ J mol^{-1}K^{-1} $\times 298$ K

$= -5156700 + 5000 = -5151700$ J mol^{-1} $= -5151.7$ kJ mol^{-1}.

Number of moles of naphthalene burnt $= 120\times10^{-3}/128 = 9.375\times10^{-4}$

Thus, amount of heat released $= 5151.7 \times 9.375\times10^{-4} = 4.830$ kJ

This caused a temperature rise of 3.05 K, thus the calorimeter constant of the bomb is $4.830/3.05 = 1.584$ kJ K^{-1}

c) $C_6H_5OH(s) + 7\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 3\ H_2O\ (l)$

Temperature rise is 2.05K, so heat released = calorimeter constant $\times\ \Delta T$

$= 1.584$ kJ K^{-1} $\times\ 2.05$ K $= 3.247$ kJ

No. of moles of phenol burnt $= 100\times10^{-3}/94 = 1.0638\times10^{-3}$ mol

Thus, $\Delta_r U = -3.247/1.0638 \times 10^{-3} = -3052.5$ kJ mol^{-1}

$\Delta_r H = \Delta_r U + \Delta_r n.R.T$

$= -3052500$ J mol^{-1} $+ (6-7) \times 8.314$ J mol^{-1}K^{-1} $\times 298$ K $= -3052500 - 2500$

$= -3055000$ J mol^{-1} $= -3055.0$ kJ mol^{-1}

$\Delta_r H^o$ = Sum for products of ($\nu \times \Delta_f H^o$) - Sum for reactants of ($\nu \times \Delta_f H^o$)

$= 6 \times -393.5 + 3 \times -285.8 - (1 \times \Delta_f H^o$ (phenol (s)) $+ 7 \times 0) = -3055$ kJ mol^{-1}

Thus $\Delta_f H^o$ (phenol (s)) $= -3055 - (-2361 - 857.4) = +163.4$ kJ mol^{-1}

Jan 2012, Q1

Using an enzyme to catalyse the organic half-reaction on the surface of a graphite electrode, a cell has been run with the cell reaction:

2-propanol (aq) ==== propanone (aq) + H_2 (g)

and E^o_{cell} has been found to be +0.29 V.

a) Write out the two half reactions in this cell, and explain what their E^o values would be. [4]
b) Draw a diagram indicating the key features this cell would have. [5]
c) Calculate Δ_rG^o for the cell reaction. [5]
d) It is already known that Δ_fG^o for propanone (aq) is -161 kJ mol^{-1}. Calculate Δ_fG^o for 2-propanol (aq). [6]
e) How would you use this Δ_fG^o and other values to calculate Δ_rG^o for the oxidation of 2-propanol to propanone by O_2? [5].

Answer outline:-
a) propanone (aq) + 2 H^+ (aq) + 2e^- === 2-propanol (aq)
2 H^+ (aq) + 2e^- === H_2 (g)
The cell reaction is exactly the reverse of that for the cell that defines the E^o value for propanone/propanol, so this is just -0.29 V. The other half reaction is of course that of the standard hydrogen electrode, so by definition $E^o = 0$.
b) The diagram should show two half cells. One with Pt electrode, aqueous H^+ electrolyte and H_2 bubbled over electrode. The other with C electrode (acceptable if don't mark enzyme on surface), and electrolyte with dissolved propanone, propanol and H^+. Salt bridge connecting them, and electrical connection between the electrodes.

c) $\Delta_rG^o = -n.F.E^o_{cell} = -2 \times 9.648 \times 10^4 \text{ J V}^{-1}\text{mol}^{-1} \times 0.29 \text{ V}$
$= -56000 \text{ J mol}^{-1} = -56 \text{ kJ mol}^{-1}$
d) For this reaction, we will have:
$\Delta_rG^o = \Delta_fG^o$ (propanone) + Δ_fG^o (H_2) - Δ_fG^o (propanol)
So: Δ_fG^o (propanol) = Δ_fG^o (propanone) + Δ_fG^o (H_2) - Δ_rG^o
$= -161 \text{ kJ mol}^{-1} + 0 + 56 \text{ kJ mol}^{-1} = -105 \text{ kJ mol}^{-1}$

e) The reaction is now: 2-propanol (aq) + 0.5 O_2 (g) ==== propanone (aq) + H_2O (l)
For this reaction $\Delta_rG^o = \Delta_fG^o$ (propanone) + Δ_fG^o (H_2O) - Δ_fG^o (propanol)
(Δ_fG^o (O_2 (g)) is zero again, element in standard state)
We need the value of Δ_fG^o (H_2O) and then we can complete the calculation.

Jan 2012, Q2

a) Show how you can write an equation for the relationship between vapour pressure of a pure substance and its $\Delta_{vap}H^o$ and $\Delta_{vap}S^o$. [4]
b) State Trouton's rule for $\Delta_{vap}S^o$. [2]
c) The boiling point of t-butylbenzene is 169 °C at 1 bar pressure. Estimate the boiling point at 0.01 bar pressure, noting the approximations and assumptions you need to make. [10]
d) Measurements of heat capacity can be used to estimate more accurately how vapour pressure depends on temperature. Draw one or more thermodynamic cycles showing how you could use this data, explaining how they work, and outline the calculations you would perform based on the cycle. [9]

Outline answer.
a) Since the formula list now gives:

$$\ln K = \frac{-\Delta H^o}{R.T} + \frac{\Delta S^o}{R}$$

it is sufficient to point out that vapourisation can be seen as an equilibrium between the pure liquid, activity = 1, and the vapour, activity = pressure (to a good approximation). Hence we replace K with p, and the entropy and enthalpy changes are for vaporisation:-

$$\ln p_{vap} = \frac{-\Delta_{vap}H^o}{RT} + \frac{\Delta_{vap}S^o}{R}$$

b) $\Delta_{vap}S^o$ for non-polar or weakly polar molecules is 80-90 J $mol^{-1}K^{-1}$. (Equivalent statements of numerical value OK, such as around 88).

c) We will assume butylbenzene follows Trouton's rule and take $\Delta_{vap}S^o$ as say 88 J $mol^{-1}K^{-1}$. (Full credit for starting from any other value, provided this is clearly stated).
At 169 °C (442 K) we have $\Delta_{vap}G^o = 0$, hence
$\Delta_{vap}H^o = T.\Delta_{vap}S^o = 442 \text{ K} \times 88 \text{ J mol}^{-1}\text{K}^{-1} = 38900 \text{ J mol}^{-1}$.
We now have to assume that both $\Delta_{vap}H^o$ and $\Delta_{vap}S^o$ are independent of temperature, so we can use the equation above. Substituting p = 0.01 bar, we get

$$\ln 0.01 = \frac{-38900 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times T_b} + \frac{88 \text{ J mol}^{-1}\text{K}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1}}$$

$$-4.605 = \frac{-4680K}{T_b} + 10.585$$

$T_b = 4680 \text{ K}/(10.585 + 4.605) = 308 \text{ K} = 35$ °C.

d) The cycles should show heating or cooling butylbenzene in both liquid and gas states between a temperature of interest and another at which the enthalpy and entropy of vapourisation are assumed known (e.g. the normal boiling point). Then the enthalpy change on heating is calculated as $C_p.\Delta T$, while the entropy change is calculated as $C_p\ln(T_2/T_1)$ – with in each case different values for the liquid and gas. Thus $\Delta_{vap}H^o$ and $\Delta_{vap}S^o$ are estimated at the temperature of interest via the cycle, and p estimated using the equation above.

Aug 2012, Q1

a) To identify the direction of a spontaneous change we can look for the direction that gives an increase in entropy or a decrease in Gibbs energy. Explain how these two apparently different criteria actually amount to the same thing, noting the relationship between entropy, enthalpy and Gibbs energy. State why Gibbs energy is such a useful function in chemistry. [7]

Here are some standard values for 25 °C:

	$\Delta_f H^o$/kJ mol^{-1}	S^o/J K^{-1}mol^{-1}
NO (g)	90.25	210.76
NO_2 (g)	33.18	240.06
SO_2 (g)	-296.83	248.22
SO_3 (g)	-395.72	256.76

b) For the reaction: NO_2 (g) + SO_2 (g) === NO (g) + SO_3 (g)
Calculate $\Delta_r H^o$ and $\Delta_r S^o$.
Hence calculate $\Delta_r G^o$ and the equilibrium constant at 25 °C. [10]

c) In a closed vessel at 25 °C the following partial pressures of gas are present:- NO, 0.7 bar; NO_2, 10^{-6} bar; SO_2 , 0.005 bar; SO_3, 0.05 bar.
Calculate $\Delta_r G$ for the same reaction in this vessel, and hence state which direction will be spontaneous. [8]

Outline Answer:

a) For a process to be spontaneous, it must lead to an increase in the entropy of the universe. But in chemistry, we usually consider changes taking place inside a closed isothermal system, and heat transferred to or from the surroundings causes changes in their entropy. At constant pressure the heat transferred in is given by ΔH of the system, and the change in entropy of the surroundings due to this transfer is thus $-\Delta H/T$. This must be added to ΔS within the system to get the total entropy change of the universe. Since for changes within the system we have: $\Delta G = \Delta H - T.\Delta S$, a negative ΔG within the system corresponds to a positive ΔS of the universe. Hence both indicate the same direction for spontaneous change. The use of ΔG allows us to determine effects on the entropy of the universe by considering only changes within the system, which is very convenient for chemistry.

b) Reaction: NO_2 (g) + SO_2 (g) === NO (g) + SO_3 (g)

Δ_rH^o = Sum for products of ($\nu \times \Delta_fH^o$) - Sum for reactants of ($\nu \times \Delta_fH^o$)
= 90.25 - 395.72 – (33.18 - 296.83) = -41.82 kJ mol^{-1}
Δ_rS^o = Sum for products of ($\nu \times S^o$) - Sum for reactants of ($\nu \times S^o$)
= 210.76 + 256.76 – (240.06 + 248.22) = –20.76 J $mol^{-1}K^{-1}$

$\Delta_rG^o = \Delta_rH^o - T.\Delta_rS^o$
Δ_rG^o = –41820 J mol^{-1} - (298K × –20.76 J $mol^{-1}K^{-1}$) = –35630 J mol^{-1}
= –35.63 kJ mol^{-1}

$\Delta_rG^o = -R.T.\ln K$

$$\ln K = \frac{-\Delta_r G^o}{R.T} = \frac{35630 Jmol^{-1}}{8.314 Jmol^{-1}K^{-1} \times 298K} = 14.38$$

$K = 1.76 \times 10^6$

c) $\Delta_rG = \Delta_rG^o + RT\ln Q$

For this reaction

$$Q = \frac{p_{NO}p_{SO_3}}{p_{NO_2}p_{SO_2}} = \frac{0.7 \times 0.05}{10^{-6} \times 0.005} = 7 \times 10^6$$

Δ_rG = -35630 J mol^{-1} + 8.314 J $mol^{-1}K^{-1}$ × 298 K × ln (7 × 10^6)
= -35630 + 39050 = +3420 J mol^{-1} = +3.42 kJ mol^{-1}
Hence the reaction will not be spontaneous as written, but will actually tend to proceed backwards, despite the large negative Δ_rG^o.

Aug 2012, Q2

a) There are several possible routes to the estimation of Gibbs energy changes in a reaction. Three of them are based on measurements: i) of composition of equilibrium mixtures; ii) in electrochemical cells; and iii) in calorimeters. For each case, outline what would be measured and what calculations would be performed to obtain a Δ_rG^o value. Note any restrictions about the type of reaction to which they can be applied. [12]

b) For the hydrocracking reaction $C_4H_{10} + H_2 === 2\ C_2H_6$, the following pressures were measured in an equilibrium mixture at 25 °C: C_4H_{10} 0.00053 bar; H_2 3.6×10^{-7} bar, C_2H_6 0.25 bar. Calculate the equilibrium constant and hence Δ_rG^o. [7]

c) For the electrochemical cell
$Pt|Fe^{2+}$ (aq), Fe^{3+} (aq)$||Cu^{2+}$ (aq)$|Cu$ $E^o_{cell} = -0.25$ V
Write out the cell reaction and calculate its Δ_rG^o value. [6]

Answer outline:-

a) (i) Measure partial pressures or concentrations, hence calculate K, and then $\Delta_rG^o = -RT\ln K$. Requires that K not be too large or too small, so all species can be measured.

(ii) Measure cell potential under standard conditions (or extrapolate to these), then calculate $\Delta_rG^o = -nFE^o_{cell}$. Only applicable to redox reactions that can be made to occur electrochemically in a reversible cell.

(iii) Determine Δ_rH^o, either directly, or via combination of other reactions (e.g. combustion of all species involved in reaction of interest). Determine S^o for each species by measuring heat input while bringing from 0 K to 298K, using $dS = dq_{in}/T$. Hence calculate Δ_rS^o by difference. Finally $\Delta_rG^o = \Delta_rH^o - T.\Delta_rS^o$. In principle applicable generally – but bonus for noting limitations such as residual 0K entropies (further reading).

b)

$$K = \frac{p^2_{C_2H_6}}{p_{C_4H_{10}}.p_{H_2}} = \frac{0.25^2}{0.00053 \times 3.6 \times 10^{-7}} = 3.3 \times 10^8$$

$\Delta_rG^o = -RT\ln K = -8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 298\ \text{K} \times \ln(3.3 \times 10^8) = -48600\ \text{J mol}^{-1}$
$= -48.6\ \text{kJ mol}^{-1}$

c)

$2\ Fe^{2+}\ (aq) + Cu^{2+}\ (aq) === 2\ Fe^{3+}\ (aq) + Cu\ (s)$

$\Delta_rG^o = -nFE^o_{cell} = -2 \times 9.648 \times 10^4\ \text{J V}^{-1}\text{mol}^{-1} \times -0.25\ \text{V}$
$= +48200\ \text{J mol}^{-1} = +48.2\ \text{kJ mol}^{-1}$

Jan 2011

Q1.

a) State the equation that relates the actual Δ_rG with its value when all reactants are in their standard states. [2]

b) State how Gibbs energy changes show the direction of spontaneous reaction, and hence explain how the relationship between Gibbs energy changes and equilibrium constant can be obtained from the equation given in part a. [7]

The equilibrium constant in water at 25 ºC has been measured to be 250 for the redox reaction: $2\ Fe^{3+}$ + p-hydroquinone ==== $2\ Fe^{2+}$ + p-quinone + $2\ H^+$
The E^o value for the Fe^{3+}/Fe^{2+} couple is known to be +0.771 V.

c) Calculate Δ_rG^o for this reaction. [5]

d) Calculate E^o_{cell} for the reaction. [5]

e) Calculate E^o for the p-quinone/p-hydroquinone couple. [6]

a) $\Delta_r G = \Delta_r G^\theta + R.T.\ln Q$

b) The spontaneous direction of reaction is always that in which $\Delta_r G$ *is negative. The reaction will continue in this direction, causing Q to change, until* $\Delta_r G$ *becomes equal to zero. The change in Q as the reaction proceeds also brings it closer to the equilibrium constant K, and eventually the two become equal. Then we can substitute in the equation above,* $\Delta_r G = 0$, *and Q = K. Hence* $0 = \Delta_r G^\theta + R.T.\ln K$, *which is rearranged to* $\Delta_r G^\theta = -R.T.\ln K$.

c) Using the equation just derived,
$\Delta_r G^o = -RT\ln K = -8.314\ J\ mol^{-1}K^{-1} \times\ 298\ K \times \ln 250 = -13680\ J\ mol^{-1}$

d) $\Delta_r G^o = -n.F.E^o_{cell}$, hence $E^o_{cell} = -\Delta_r G^o/n.F$
$E^o_{cell} = +13680\ J\ mol^{-1}/(2 \times 96480\ J\ V^{-1}mol^{-1}) = +0.071\ V$

e) $E^o_{cell} = E^o$ (cathode) $-$ E^o (anode)
$E^o_{cell} = E^o (Fe^{3+}/Fe^{2+}) - E^o$ (p-quinone/p-hydroquinone)
$0.071V = 0.771\ V - E^o$ (p-quinone/p-hydroquinone)
E^o (p-quinone/p-hydroquinone) $= -0.071V + 0.771\ V = 0.700\ V$

Q2.
a) Explain the principles behind the use of thermodynamic cycles. In your answer, make sure you include explanations of: i) why they work; ii) what properties they can be used for; and iii) why they are useful. [7]

The reaction: ethene (g) + H_2O (g) ==== ethanol (g)
has $\Delta_r S^o = -130\ J\ mol^{-1}K^{-1}$ at 380 K. The following constant pressure heat capacities are also known: ethene (g) $43.6\ J\ mol^{-1}K^{-1}$; H_2O (g) $33.6\ J\ mol^{-1}K^{-1}$; ethanol (g) $65.4\ J\ mol^{-1}K^{-1}$.

b) Draw a thermodynamic cycle that would allow you to estimate $\Delta_r S^o$ at 500 K. Then use it to make the estimate. [8]

c) $\Delta_r H^o$ for the same reaction at 500 K has been estimated to be $-45.6\ kJ\ mol^{-1}$. Estimate $\Delta_r G^o$. [5]

d) Hence estimate the equilibrium constant. [5]

a) Thermodynamic cycles can be constructed for any thermodynamic function of state. If we go round a series of reactions or other processes such that we finally end up in exactly the same state as we started in, then any function of state cannot change as we go round the cycle. Hence the sum of changes in the individual reactions or processes must be zero. If we know the changes associated with all but one of the steps, we can calculate the change in the missing one. Often we can find a way to go between a starting and end state of interest via a roundabout route, but where the changes in properties for each step are either known or can be easily estimated. Hence we calculate the value we want for the direct change. Useful thermodynamic functions of state include internal energy, enthalpy, entropy and Gibbs energy.

b) The cycle should show the reaction at 380 K, the reaction at 500K, and joining them the steps of cooling the starting materials from 500K to 380K, then heating the products back up to 500K. For the heating and cooling steps we have

$$\Delta S = \int_{start}^{end} \frac{dq_{in,rev}}{T} = \int_{T_1}^{T_2} \frac{C_p.dT}{T} = C_p.(\ln T_2 - \ln T_1) = C_p.\ln\left(\frac{T_2}{T_1}\right)$$

assuming C_p values are independent of temperature, as the question implies.
Hence for cooling the starting materials per mole of reaction (i.e. 1 mole each of ethene and H_2O)

$\Delta S = 43.6 \text{ J mol}^{-1}\text{K}^{-1} \times \ln(380/500) + 33.6 \text{ J mol}^{-1}\text{K}^{-1} \times \ln(380/500)$
$= -21.2 \text{ J mol}^{-1}\text{K}^{-1}$

while for heating the product ethanol

$\Delta S = 65.4 \text{ J mol}^{-1}\text{K}^{-1} \times \ln(500/380) = 17.9 \text{ J mol}^{-1}\text{K}^{-1}$

Hence for reaction at 500K

$\Delta_r S^o = -21.2 \text{ J mol}^{-1}\text{K}^{-1} - 130 \text{ J mol}^{-1}\text{K}^{-1} + 17.9 \text{ J mol}^{-1}\text{K}^{-1} = -133.3 \text{ J mol}^{-1}\text{K}^{-1}$

c) $\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o = -45600 \text{ J mol}^{-1} - 500\text{K} \times -133.3 \text{ J mol}^{-1}\text{K}^{-1}$
$= +21050 \text{ J mol}^{-1}$

d) $\ln K = -\Delta_r G^o/RT = -21050 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 500 \text{ K}) = -5.06$
$K = 6.32 \times 10^{-3}$ (optionally with units bar^{-1})

August 2011

Q1:

a) Outline the principles of the procedure for using a bomb calorimeter to measure the heat released on combustion of an organic compound. [5]

b) 53.0 mg of beta-glucose ($C_6H_{12}O_6$) are burnt in a bomb with a calorimeter constant (sometimes known as heat capacity) of 495 J K^{-1}. The temperature rises from the initial value of 25 °C by 1.67 K. Calculate the change in internal energy due to combustion per mole of glucose. [7]

c) Explain why in this case the values of ΔU and ΔH are almost identical. [3]

d) The $\Delta_f H^o$ values are known to be -285.8 kJ mol^{-1} for H_2O (l) and -393.5 kJ mol^{-1} for CO_2 (g). Estimate $\Delta_f H^o$ for beta-glucose. [5]

e) Explain why it is useful to have tables of $\Delta_f H^o$ values for compounds. [5]

a) A known mass of the compound is placed in the sample cup, the bomb is sealed, filled with O_2 under pressure, and equilibrated in the water bath at the desired initial temperature, the whole apparatus being insulated from heat loss or gain. Then the sample is ignited and allowed to burn completely. The temperature increase of the water bath due to the heat liberated is recorded. The water bath is then cooled back down to the original temperature, then heated back up electrically to the same final temperature as before. The amount of energy required is measured electrically, and is equal to that released on combustion of the known mass of sample. Alternatively, the calorimeter constant (heat required to heat it per degree) may be known from previous measurements.

b) Heat released = calorimeter constant × $\Delta T = 495 \text{ J K}^{-1} \times 1.67 \text{ K} = 826.7 \text{ J}$
Formula weight of glucose = $(6 \times 12) + 12 + (6 \times 16) = 180$
Moles of glucose burnt = $(53 \times 10^{-3})/180 = 2.944 \times 10^{-4}$
In the constant volume bomb calorimeter there is no work, so ΔU is equal to the heat released, with negative sign (heat in is positive)
$\Delta U = -826.7/2.944 \times 10^{-4} = -2808000 \text{ J mol}^{-1} = -2808 \text{ kJ mol}^{-1}$

c) *The difference between these two in a constant pressure process would be given by $\Delta H = \Delta U + p.\Delta V$. The $p.\Delta V$ term is only significant when there is a change in the number of moles of gas as a result of the reaction. In this case the combustion reaction is:*
$C_6H_{12}O_6$ (s) + 6 O_2 (g) === 6 CO_2 (g) + 6 H_2O (l)
so there is no change in the number of moles of gas.

d) We consider the combustion reaction and use
$\Delta_r H^o$ = Sum for products of ($\nu \times \Delta_f H^o$) - Sum for reactants of ($\nu \times \Delta_f H^o$)
$-2812 \text{ kJ mol}^{-1} = (6 \times -393.5) + (6 \times -285.8) - (1 \times \Delta_f H^o \text{ (beta-glucose)} + 6 \times 0) \text{ kJ mol}^{-1}$
$\Delta_f H^o$ (beta-glucose) = $+2808 + (6 \times -393.5) + (6 \times -285.8) \text{ kJ mol}^{-1} = -1268 \text{ kJ mol}^{-1}$

Q2:
a) Explain the concept of thermodynamic activities. Include an explanation of how activities can be estimated for: i) pure solids; ii) pure liquids; iii) gases; and iv) molecules in solution. [7]

The following electrochemical cell is being studied at 25 °C:

$Cu|CuSO_4$ (0.1 M, aq)||Cl^-(aq, a=1)|AgCl(s)|Ag
At balance the Cu electrode is measured to have a potential of +0.064 V relative to the Ag electrode.
The following values are known:

Cu^{2+}/Cu	$E^o = +0.337$ V
$AgCl/Ag + Cl^-$	$E^o = +0.220$ V

b) Write out the cell reaction and state the value of E_{cell}. [3]

c) Calculate E^o_{cell}. [5]

d) Calculate the activity of Cu^{2+} ions in 0.1 M CuSO4 solution. [7]

e) Calculate the activity coefficient for Cu^{2+} ions in this solution, and comment on the value. [3]

a) The activity of a chemical species is a measure of its thermodynamic tendency to participate in a chemical reaction. The higher the activity, the less positive or more negative will be the Gibbs energy change of any reaction that consumes it. So activities should be used in the completely correct expressions for the equilibrium constant K or reaction quotient Q. The activity of a pure solid or liquid phase can be taken as 1, regardless of how much is present – this is the origin of the elementary rule that they are left out of equilibrium constant expressions. The activity of a gas is very well approximated by its partial pressure in bar (except at very high pressures). For a species in solution, the activity can be taken as the product of an activity coefficient and the molar concentration. As the solution becomes more and more dilute, the activity coefficient becomes ever closer to 1 – this is the reason that molar concentrations are commonly used in elementary level equilibrium constants.

b) $Cu + 2\ AgCl\ (s) === Cu^{2+}\ (aq) + 2\ Ag + 2\ Cl^-\ (aq)$
E_{cell} corresponds to the relative potential of the right hand electrode in cell notation, so is –0.064V.

c) $E^o_{cell} = E^o\ (\text{cathode}) - E^o\ (\text{anode}) = E^o\ (AgCl/Ag + Cl^-) - E^o\ (Cu^{2+}/Cu)$
$= 0.220 – 0.337 = –0.117$ V

d) $$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q$$

$$\ln Q = \frac{nF}{RT}(E^o_{cell} - E_{cell}) = \frac{2\times 96480 JV^{-1}mol^{-1}}{8.314 Jmol^{-1}K^{-1}\times 298K}(-0.117V + 0.064V) = -4.13$$

Q=0.0161
For the cell reaction above

$$Q = \frac{a_{Cu^{2+}}.a_{Ag}^{2}a_{Cl^{-}}^{2}}{a_{Cu}.a_{AgCl}^{2}} = \frac{a_{Cu^{2+}} \times 1^2 \times 1^2}{1 \times 1^2} = a_{Cu^{2+}} = 0.0161$$

e) *Activity = activity coefficient × concentration, so*
activity coefficient = activity/concentration = 0.0161/0.1 = 0.161
This value is very much less than 1, which it would be equal to in very dilute solution. Such a difference even at 0.1 M concentration is because Cu^{2+} *is an ion.*

May 2010, Q1

a) State the 3rd Law of Thermodynamics. Why is the 3rd Law necessary in order to be able to measure a value for the entropy of a substance at a specified pressure and temperature? [6]

b) For elements in their standard states, the values of $\Delta_f H^o$ and $\Delta_f G^o$ are zero, but the values of S^o are not. Explain why there is this difference. [5]

c) The entropy of H_2O (s) at 200K is 30.4 J $mol^{-1}K^{-1}$. From this temperature up to the melting point the constant pressure heat capacity of ice may be taken as 35 J $mol^{-1}K^{-1}$, while for liquid water the heat capacity can be taken as 75 J $mol^{-1}K^{-1}$. The enthalpy of fusion of H_2O at 273 K is 6.008 kJ mol^{-1}. Estimate the entropy of H_2O (l) at 25 °C. [9]

d) Here are three other entropy values for 25 °C:

	S^o/J $K^{-1}mol^{-1}$
Zn (s)	41.6
ZnO (s)	43.6
H_2 (g)	130.7

Calculate $\Delta_r S^o$ for: Zn (s) + H_2O (l) ==== ZnO (s) + H_2 (g) [5]

a) *The entropy of all pure perfect crystalline substances is zero at 0 K. Other relationships only allow changes in entropy to be measured. In order to give an absolute value it is necessary to have a value for some specified reference state, and the 3rd Law offers this. The most obvious use is then to calculate entropy changes (via heat capacity measurements) on heating from 0 K to the conditions of interest.*

b) *With H and G we have the same problem that only changes can be measured. But in this case there is no meaningful way to set a zero. Hence the use of enthalpies* *and Gibbs energies of formation, with the arbitrary but conventional definition of these as zero for elements in their standard states. The 3rd Law allows absolute values of entropies – which are then non-zero for elements at their usual standard state temperatures.*

c) *Calculate entropy increases for each part of the heating process, using*

ΔS for heating a single phase = $C_p.\ln(T_2/T_1)$
ΔS for phase change = ΔH phase change/T

Entropy of solid H_2O at 200K	30.4 J $mol^{-1}K^{-1}$
Heat solid H_2O from 200 K to 273 K:	
$\Delta S = C_p.\ln(T_2/T_1) = 35$ J $mol^{-1}K^{-1} \times \ln(273/200)$ =	10.9 J $mol^{-1}K^{-1}$
Melt H_2O at 273 K	
$\Delta_{fus}S = \Delta_{fus}H/T_{fus} = 6008$ J $mol^{-1}/273$ K =	22.0 J $mol^{-1}K^{-1}$
Heat liquid H_2O from 273 K to 298 K:	
$\Delta S = C_p.\ln(T_2/T_1) = 75$ J $mol^{-1}K^{-1} \times \ln(298/273)$ =	6.6 J $mol^{-1}K^{-1}$
Total = 69.9 J $mol^{-1}K^{-1}$	

d) $\Delta_r S^o = S^o(ZnO) + S^o(H_2) - S^o(Zn) - S^o(H_2O)$
$= 43.6 + 130.7 - 41.6 - 69.9 = +62.8$ J $mol^{-1}K^{-1}$

May 2010, Q2.

a) In any spontaneous process the entropy of the universe increases. A thermodynamically reversible process can be defined as one in which the entropy of the universe stays the same. Is it possible for a thermodynamically reversible process to take place? If not, why is the concept of thermodynamic reversibility useful in understanding real systems? [6]

b) Explain how an electrochemical cell can come near to operating as thermodynamically reversible. [3]

c) An electrochemical cell is written as:

$Pt|Fe^{3+}(aq, a=1), Fe^{2+}(aq, a=1)||Cl^-(aq, a=1)|AgCl(s)|Ag(s)$

Write out the equation for the cell reaction, and the equations for the two half reactions. [3]

d) This cell is found to have a potential of -0.55 V. E° for the AgCl/Ag + Cl^- couple is known to be +0.22 V. Calculate E° for the Fe^{3+}/Fe^{2+} couple. [6]

e) What would be the cell potential if the activity of Fe^{2+} in the left hand half-cell was reduced to 0.01. [7]

a) Idea of thermodynamically reversible process as limit we can never quite reach, but can in principle come as close to as we wish – would have to be infinitely slow, with infinitesimal driving forces, so that increase in entropy of universe is minimal. The concept of the reversible limit is useful in that it allows the definition of entropy changes in terms of heat transfers, and can be used in thermodynamic cycles and related reasoning. The nature of thermodynamic cycles means we don't have to carry out all the stages experimentally.

b) If we impose a potential that exactly balances the cell potential, no current flows and no reactions happen. If we now raise or lower the applied potential infinitesimally, a tiny current flows, work is done, and the cell reaction advances (very slowly) in one direction. Now switch the potential just the other side of balance, and everything reverses, with all changes being almost exactly reversed, and almost zero overall entropy change.

c) Fe^{2+} (aq) + AgCl(s) ==== Fe^{3+} (aq) + Ag(s) + Cl^- (aq)
Fe^{3+} (aq) + e^- ==== Fe^{2+} (aq)
AgCl(s) + e^- ==== Ag(s) + Cl^- (aq)

d) This cell is operating under standard conditions, so we can use
$E^o_{cell} = E^o$ (cathode) - E^o (anode)
$E^o_{cell} = E^o$ (AgCl/Ag + Cl^-) - E^o (Fe^{3+}/ Fe^{2+})
-0.55 V = +0.22 V - E^o (Fe^{3+}/ Fe^{2+})
E^o (Fe^{3+}/ Fe^{2+}) = +0.55 V + 0.22 V = + 0.77 V

e) We use the Nernst equation:

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q = -0.55V - \frac{RT}{F}\ln\frac{a_{Fe^{3+}}a_{Ag}a_{Cl^-}}{a_{Fe^{2+}}a_{AgCl}} = -0.55V - \frac{RT}{F}\ln\frac{1\times1\times1}{0.01\times1}$$

$$E_{cell} = -0.55V - \frac{8.314Jmol^{-1}K^{-1}\times298K}{96500JV^{-1}mol^{-1}}\times\ln(100) = -0.55 - 0.12 = -0.67V$$

Aug 2010, Q1

a) Explain the concept of a thermodynamic cycle, including how and why it works for thermodynamic calculations. Explain also why thermodynamic cycles are so useful for calculations in chemistry. [7]

b) Here are some Gibbs energies of formation for 25 °C:-

	$\Delta_f G^o$/kJ mol^{-1}
HCHO (g)	-102.5
CH_3CHO (l)	-128.1
CH_3OH (l)	-166.3
CH_3CH_2OH (l)	-174.8

Draw out a thermodynamic cycle that would allow you to calculate Δ_rG^o for the reaction below, and use it to obtain the answer:
CH_3OH (l) + CH_3CHO (l) ==== HCHO (g) + CH_3CH_2OH (l) [7]

c) Calculate Keq for this reaction. [5]

d) State the relationship between the changes in Gibbs energy, entropy and enthalpy in a reaction. Explain why the Gibbs energy change summarises the consequences of the second law of thermodynamics for the spontaneous direction of reaction. [6]

a) Thermodynamic cycles can be constructed for any thermodynamic function of state. If we go round a series of reactions or other processes such that we finally end up in exactly the same state as we started in, then any function of state cannot change as we go round the cycle. Hence the sum of changes in the individual reactions or processes must be zero. If we know the changes associated with all but one of the steps, we can calculate the change in the missing one. Often we can find a way to go between a starting and end state of interest via a roundabout route, but where the changes in properties for each step are either known or can be easily estimated. Hence we calculate the value we want for the direct change.

b) Cycle should show decomposition ("unformation") of starting materials into elements, then formation of products from these same elements. Hence we find that
$\Delta_rG^o = \Delta_fG^o(HCHO) + \Delta_fG^o(CH_3CH_2OH) - \Delta_fG^o(CH_3OH) - \Delta_fG^o(CH_3CHO)$
$= -102.5 - 174.8 + 166.3 + 128.1$ kJ mol^{-1}
$= +17.1$ kJ mol^{-1}

c) $\Delta_rG^o = -RT \ln K$
Hence, $\ln K = -\Delta_rG^o/RT$
$= -17100 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}) = -6.902$
Thus $K = 1.01 \times 10^{-3}$

d) $\Delta G = \Delta H - T.\Delta S$.
One statement of the second law is that for a process to be spontaneous, it must lead to an increase in the entropy of the universe. But in chemistry, we usually consider changes taking place inside a closed isothermal system, and heat transferred to or from the surroundings causes changes in their entropy. At constant pressure the heat transferred in is given by ΔH of the system, and the change in entropy of the surroundings due to this transfer is thus -ΔH/T. This must be added to ΔS within the system to get the total entropy change of the universe. Since for changes within the system we have: ΔG = ΔH – T.ΔS, a negative ΔG within the system corresponds to a positive ΔS of the universe. Hence both indicate the same direction for spontaneous change. The use of ΔG allows us to determine effects on the entropy of the universe by considering only changes within the system, which is very convenient for chemistry. [Last 2 sentences not essential for full marks, not required by question].

Aug 2010, Q2

The following electrochemical cell is being studied at 25 ºC:

Pt|p-quinone (aq, a= 0.02), p-hydroquinone (aq, a= 0.04), H^+ (a = 10^{-6})||Ag^+ (aq, a=0.01)| Ag

The Eº values are:
p-quinone (aq) + 2 H^+ (aq) + 2 e^- ==== p-hydroquinone (aq) +0.700 V
Ag^+ (aq) + e^- ==== Ag (s) +0.800 V

a) Write out the cell reaction. [2]

b) Calculate E^o_{cell}. [5]

c) Calculate E_{cell}. [8]

d) Calculate the actual ΔG for the cell reaction under the conditions studied. [5]

e) Draw a diagram showing the key features of an electrochemical cell whose potential would be equal to Eº for the p-quinone/p-hydroquinone couple, indicating which electrode would give its sign to the potential. [5]

a) p-hydroquinone (aq) + 2 Ag^+ (aq) ==== p-quinone (aq) + 2 H^+ (aq) + 2 Ag (s)
(Half this equation also acceptable)

b) E^o_{cell} = Eº (cathode) - Eº (anode)
E^o_{cell} = Eº (Ag^+/Ag) - Eº (p-quinone/p-hydroquinone)
= 0.800 – 0.700 = 0.100 V

c) First calculate Q for the cell reaction in this cell.

$$Q = \frac{a_{p-quin} a^2_{H^+} a^2_{Ag}}{a_{p-hydro} a^2_{Ag^+}} = \frac{0.02 \times (10^{-6})^2 \times 1^2}{0.04 \times 0.01^2} = \frac{0.02 \times 10^{-12}}{0.04 \times 10^{-4}} = 5 \times 10^{-9}$$

Now use:

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q = 0.100V - \frac{8.314 Jmol^{-1}K^{-1} \times 298K}{2 \times 96500 JV^{-1}mol^{-1}} \times \ln(5 \times 10^{-9}) = 0.100 + 0.245 = +0.345V$$

d) ΔG = -n.F.E_{cell}
= -2 × 9.65 × 10^4 J $V^{-1}mol^{-1}$ × 0.345 V
= -66600 J mol^{-1} = -66.6 kJ mol^{-1}

e) The diagram should show: one half cell with aqueous H^+ solution (a=1), a Pt electrode, and H_2 gas bubbled over it at 1 bar pressure; the second half cell with p-quinone, p-hydroquinone and H^+ in solution, all at activity 1, and a Pt or other noble metal electrode; an electrical connection between the electrodes via a voltmeter; a salt bridge connecting the electrolytes. The sign of the potential will be that at the electrode in the p-quinone/p-hydroquinone half cell.

May 2009 Q1

a) State the equations that relate $\Delta_r G^o$ to i) the reaction equilibrium constant; and ii) the enthalpy change in the reaction. [2]

b) Combine these equations to give a relationship between equilibrium constant and temperature, stating the assumptions necessary for it to hold. State the variant of this equation that gives the vapour pressure of a liquid. [8]

c) State Trouton's rule, and comment on whether you would expect it to hold for benzyl benzoate. [3]

d) The boiling point of benzyl benzoate is reported as 170 ^{o}C at 5 mm Hg pressure. (1 bar = 750.1 mm Hg). Estimate $\Delta_{vap}H^o$ for benzyl benzoate. [6]

e) Hence estimate what would be the boiling point at 1 bar pressure. An experimental value of 320 ^{o}C has been reported. Comment on how this agrees with your prediction. [6]

Outline answer:

a) $\Delta_r G^o = -R.T.\ln K$
$\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$

b) If we assume ΔH^o and ΔS^o do not vary over the temperature range in question then:-
$-R.T.\ln K = \Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$
Divide both sides by $-R.T$ to get
$\ln K = -\Delta_r H^o/R.T. + \Delta_r S^o/R$

We can see the liquid-vapour equilibrium as a reaction, liquid === gas. Hence K = $a_{gas}/a_{liquid} = p_{vap}$. (The pure liquid has activity of 1 by definition, while that of the gas is very well approximated by the pressure of the vapour in bar.) So we can re-write the above equation as

$\ln p = -\Delta_{vap}H^o/R.T. + \Delta_{vap}S^o/R$

c) Trouton's rule states that $\Delta_{vap}S$ is 80-90 J $mol^{-1}K^{-1}$ for most/all liquids that are not strongly polar or associated. Benzyl benzoate should qualify here.

d) Re-arrange the equation to give
$\Delta_{vap}H^o = T.\Delta_{vap}S^o - R.T.\ln p$
$= 443\ K \times 85\ J\ mol^{-1}K^{-1} - 8.314\ J\ mol^{-1}K^{-1} \times 443\ K \times \ln(5/750.1)$
$= 37655\ J\ mol^{-1} - (-18455\ J\ mol^{-1}) = 56110\ J\ mol^{-1}$

e) At the normal boiling point p = 1 bar, lnp = 0, so $\Delta_{vap}H^o = T.\Delta_{vap}S^o$
(The same relationship follows by saying $\Delta_{vap}G^o = 0$)
Hence
$T_b = \Delta_{vap}H^o/\Delta_{vap}S^o$
$= 56110\ J\ mol^{-1}/85\ J\ mol^{-1}K^{-1} = 660\ K$
i.e. 387 ºC
This is quite a lot higher than the reported experimental value. Given how high this is, one possibility is that at atmospheric pressure the liquid boils with decomposition.

May 2009, Q2

a) The second law of thermodynamics states that the entropy of the universe increases in all spontaneous changes. But some spontaneous reactions proceed with substantially negative values of Δ_rS^o, e.g. 2 CO (g) + 2 NO (g) === 2 CO_2 (g) + N_2 (g) has $\Delta_rS^o = -99$ J $mol^{-1}K^{-1}$. Explain how this is still consistent with the second law. [9]

b) The reaction: ethene (g) + H_2O (l) ==== ethanol (l) is found to have an equilibrium constant (based on activities) of 10.4 at 298 K. Calculate Δ_rG^o. [5]

c) The following value is also known:
ethyl acetate (l) + H_2O (l) ==== ethanol (l) + acetic acid (l) $\Delta_rG^o = 5.2$ kJ mol^{-1}
Calculate Δ_rG^o and hence the equilibrium constant for: ethene (g) + acetic acid (l) ==== ethyl acetate (l). [8]

d) What do these values tell us about whether and when ethene and acetic acid will react spontaneously? [3]

Outline answer

a) In chemistry we normally state changes in entropy (and other thermodynamic values) for a closed system, rather than the universe. So when the example reaction proceeds, the negative value of Δ_rS^o indicates that the entropy of the system falls. Because the second law still holds, the entropy of the surroundings must have increased by a larger amount, such that the total entropy of the universe has increased. The entropy of the surroundings will have increased because of heat transferred into them from the system. In other words, the reaction must have a sufficiently negative $\Delta_r H^o$, so that enough heat is released to give the necessary increase in entropy of the surroundings. The answer may also refer to $\Delta_r G^o$, although this is not required, pointing out how, calculated as $\Delta_r H^o - T.\Delta_r S^o$, it captures this balance quantitatively, such that a negative Gibbs energy change in the system necessarily corresponds to a positive entropy change in the universe.

b) $\Delta_r G^o = -RT\ln K = -8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln 10.4 = -5800 \text{ J mol}^{-1}$

c) ethyl acetate (l) + H_2O (l) ==== ethanol (l) + acetic acid (l) $\Delta_r G^o = 5.2 \text{ kJ mol}^{-1}$
But we actually want ethyl acetate on the right hand side, so reverse, giving:
ethanol (l) + acetic acid (l) ==== ethyl acetate (l) + H_2O (l) $\Delta_r G^o = -5.2 \text{ kJ mol}^{-1}$
Now add this reaction to the one whose $\Delta_r G^o$ was calculated in (b)
ethene (g) + H_2O (l) ==== ethanol (l) $\Delta_r G^o = -5.8 \text{ kJ mol}^{-1}$
to get, after ethanol (l) and H_2O (l) have cancelled out
ethene (g) + acetic acid (l) ==== ethyl acetate (l) $\Delta_r G^o = -5.2 -5.8 = -11.0 \text{ kJ mol}^{-1}$

$\Delta_r G^o = -RT\ln K$, so
$\ln K = -\Delta_r G^o/RT = 11000 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}) = 4.4398$
$K = 84.8$

d) They tell us that the reaction will be spontaneous under standard conditions (unit activity of all 3 reactants), and also with a reasonable excess of product. However, if the reaction quotient (activity of ethyl acetate divided by activity of acetic acid and activity (or pressure) of ethane) is greater than 84.8, the forward reaction will no longer be spontaneous.

May 2008, Q1

a) A bomb calorimeter has a heat capacity of 1.374 kJ K^{-1}. Acetone (propanone, C_3H_6O (l), 210 mg) was burnt in the calorimeter, starting at 25.00 °C, and the temperature rise was 4.71K. Calculate ΔU^o and ΔH^o for combustion of acetone. [30%]

b) Explain the concept of a thermodynamic cycle in calculating changes in properties, making clear why these cycles work and how they are useful. [30%]

c) Estimate ΔH for the combustion of acetone at 273 K and 1 bar, making use of the following constant pressure heat capacities, all in $\text{J mol}^{-1} \text{K}^{-1}$: acetone (l), 124.7; O_2 (g), 29.36; H_2O (l), 75.29; CO_2 (g), 37.11. Make clear any assumptions you need to make. [40%]

Outline answer:

a) Relative molecular mass of acetone = $3 \times 12 + 6 + 16 = 58$

No. moles burnt = $210 \times 10^{-3}/58 = 3.621 \times 10^{-3}$
The total heat output was $1.374 \text{ kJ K}^{-1} \times 4.71 \text{ K} = 6.471 \text{ kJ}$
Hence heat evolved = $6.471/(3.621 \times 10^{-3}) = 1787 \text{ kJ mol}^{-1}$
The calorimeter operates at constant volume, so no work is done, and hence
$\Delta U^o = -1787 \text{ kJ mol}^{-1}$

Reaction is: $C_3H_6O\ (l) + 4\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 3\ H_2O\ (l)$
$\Delta_rH^o = \Delta_rU^o + p\Delta_rV = \Delta_rU^o + \Delta_rn.R.T$
$= -1787000 \text{ J mol}^{-1} + ((3-4) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K})$
$= -1787000 - 2500 = -1789500 \text{ J mol}^{-1} = -1789.5 \text{ kJ mol}^{-1}$
[Rounding to 4 sig figures equally if not more correct]

b) Thermodynamic cycles can be constructed for any thermodynamic function of state. If we go round a series of reactions or other processes such that we finally end up in exactly the same state as we started in, then any function of state cannot change as we go round the cycle. Hence the sum of changes in the individual reactions or processes must be zero. If we know the changes associated with all but one of the processes, we can calculate the change in the missing one. Often we can find a way to go between a starting and end state of interest via a roundabout route, but where the changes in properties for each step are either known or can be easily estimated. Hence we calculate the value we want for the direct change.

c) We could go between the same starting and final states as follows: 1) heat acetone and O_2 at constant pressure from 273 to 298 K; 2) carry out reaction at 298 K, with Δ_rH^o as calculated above; 3) cool the CO_2 and H_2O from 298 to 273K. The sum of these three must have the same ΔH as the direct combustion reaction at 273 K. To work out the ΔH for steps 1 and 3 we use the heat capacities given, which we have to assume are independent of temperature in the range 273 to 298 K (reasonably accurate). We also have to assume that the product is H_2O (l) – if it was H_2O (s) we would need to add in an extra latent heat term.

Heating, step 1: $\Delta H = 25 \text{ K} \times (124.7 \text{ J mol}^{-1} \text{ K}^{-1} + 4 \times 29.36 \text{ J mol}^{-1} \text{ K}^{-1})$
$= +6054 \text{ J mol}^{-1}$
(NB, for each mole of acetone or reaction we need to heat 4 mol O_2)
Cooling, step 3: $\Delta H = -25 \text{ K} \times (3 \times 75.29 \text{ J mol}^{-1} \text{ K}^{-1} + 3 \times 37.11 \text{ J mol}^{-1} \text{ K}^{-1})$
$= -8430 \text{ J mol}^{-1}$
Hence for the combustion at 273 K we estimate
$\Delta_rH = -1789500 + 6054 - 8430 \text{ J mol}^{-1} = -1792000 \text{ J mol}^{-1} = -1792 \text{ kJ mol}^{-1}$

May 2008, QUESTION 2

The following electrochemical cell has been studied:

Pt|O_2(g, 1 bar)|HCl (aq, pH 0)||$AgNO_3$ (0.1 M)|Ag $E_{cell} = -0.497$ V at 25 ºC

$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$ $E^o = 1.229$ V
$Ag^+ + e^- \rightarrow Ag$ $E^o = 0.800$ V

a) Write out the cell reaction, and calculate E^o_{cell}. [20%]
b) Draw a diagram showing the essential features of this cell. [20%]
c) Explain how an electrochemical cell can be used to measure the activity coefficients of ions in solution, stating the equation that relates E_{cell} and E^o_{cell}. [25%]
d) Estimate the activity and activity coefficient of Ag^+ in 0.1 M $AgNO_3$ (assume that pH 0 means that the activity of H^+ is 1). [35%]

Answer outline:-
a) $2\,H_2O + 4Ag^+\,(aq) \rightarrow O_2\,(g) + 4\,H^+\,(aq) + 4Ag\,(s)$
Also acceptable to have other multiples e.g.
$H_2O + 2Ag^+\,(aq) \rightarrow 0.5\,O_2\,(g) + 2\,H^+\,(aq) + 2Ag\,(s)$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.800 - 1.229 = -0.429$ V

b) The diagram should show: one half cell with aqueous HCl solution, a Pt electrode, and O_2 gas bubbled over it; the second half cell with Ag^+ in solution and an Ag electrode; an electrical connection between the electrodes via a voltmeter; a salt bridge connecting the electrolytes.

c) $E_{cell} = E^o_{cell} - (RT/nF)\ln Q$
If we know the standard potentials (i.e. E^o_{cell}) and we measure the cell potential under non-standard conditions, we can use this equation to calculate Q for those conditions. Q is the ratio of the activities of all species involved in the cell reaction. If all but one of these are known (e.g. by definition for solids, from pressure for gases), the remaining one can be calculated from the known value of Q. Assuming we know the molar concentration of the ion whose activity we have calculated, we obtain its activity coefficient. (The issue of single ion activities being in principle unmeasurable is beyond the scope of the class, but credit will be given to any student who mentions it from further reading.)

d) For the cell reaction in this case we re-arrange the equation above to get
$\ln Q = (nF/RT)(E^o_{cell} - E_{cell})$
then substitute to get

$$\ln Q = \frac{4 \times 9.648 \times 10^4\, JV^{-1}mol^{-1}}{8.314 Jmol^{-1}K^{-1} \times 298K} \times (-0.429V - -0.497V) = 155.8V^{-1} \times 0.068V = 10.59$$

Hence $Q = 3.982 \times 10^4$
For this cell reaction

$$Q = \frac{a_{O_2} . a^4_{H^+} a^4_{Ag} .}{. a^2_{H_2O} . a^4_{Ag^+}} \approx \frac{1 \times 1^4 \times 1^4}{1^2 \times a^4_{Ag^+}}$$

Here we have taken all but one of the activities as equal to 1: of O_2 gas at 1 bar pressure, of H^+ as told in the question, of pure solid Ag (standard state), and of the solvent water (in dilute solution its activity is almost the same as pure water).

Hence $(a_{Ag}+)^4 \approx 1/Q = 2.512 \times 10^{-5}$
and $a_{Ag}+ = 0.0708$
We know that its concentration = 0.1 M, hence its activity coefficient is 0.708.

May 2006 - QUESTION 1
Sketch the main features of a bomb calorimeter and describe how it is used. [8]

In a bomb calorimeter, when 240 mg of naphthalene ($C_{10}H_8$(s); relative mass 128) were burned in a bomb calorimeter the temperature rose by 6.10 K. Using this information calculate the heat capacity of the calorimeter. When 200 mg of phenol (C_6H_5OH(s); relative molecular mass 94) were burned under the same conditions the rise in temperature was 4.10 K. Calculate the value of $\Delta H^o_{f,298}$ (phenol). [12]
[$\Delta H^o_{f,298}$ (kJ mol^{-1}) values are 78.5, -393.5 and -285.8 for $C_{10}H_8$(s), CO_2 (g) and H_2O (l), respectively. R is 8.314 J mol^{-1} K^{-1}]

Outline answer:
The key features of a bomb calorimeter should be noted in a sketch and these include: very accurate thermometer, ignition coil, steel bomb with screw-top lid, water bath, inlet for high pressure of oxygen to fill the bomb prior to ignition. A typical operation procedure should be reported including: (i) accurate weighing of sample for combustion, (ii) accurate measurement of water bath temperature, T_i, (iii) filling up bomb with excess of oxygen and, after ignition, (iv) accurate measurement of final water bath temperature T_f. The use of an electrical heater to determine the heat evolved by the system that causes a change in temperature, $T_f - T_i$, should then be briefly discussed. (Electrical energy expended by the heater = volts × current × time)

$$C_{10}H_8(s) + 12\ O_2\ (g) \rightarrow 10CO_2\ (g) + 4\ H_2O\ (l)$$

$\Delta_r H^o$ = Sum for products of $(\nu \times \Delta_f H^o)$ - Sum for reactants of $(\nu \times \Delta_f H^o)$
$= (10 \times -393.5 + 4 \times -285.8) - (1 \times 78.5 + 12 \times 0) = -5156.7$ kJ mol^{-1}

but the heat evolved in the constant volume calorimeter will be Δ_rU^o rather than Δ_rH^o, so we calculate by

$\Delta_rU^o = \Delta_rH^o - p\Delta_rV = \Delta_rH^o - \Delta_rn.R.T$

$= -5156700 \text{ J mol}^{-1} - (10-12) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}$

$= -5156700 + 5000 \text{ J mol}^{-1} = -5151.7 \text{ kJ mol}^{-1}$

Number of moles of naphthalene burnt = $240\times10^{-3}/128 = 1.875\times10^{-3}$

Thus, amount of heat released = $5151.7 \text{ kJ mol}^{-1} \times 1.875\times10^{-3} \text{ mol} = 9.659 \text{ kJ}$

Heat released = Heat capacity (or calorimeter constant) of bomb (Q) × Rise in temperature (ΔT)

$Q = \text{Heat released}/\Delta T = 9.659 \text{ kJ} / 6.10 \text{ K} = 1.584 \text{ kJ K}^{-1}$

In the phenol reaction

$$C_6H_5OH(s) + 7\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 3\ H_2O\ (l)$$

Heat released = $Q \times \Delta T = 1.584 \text{ kJ K}^{-1} \times 4.10 \text{ K} = 6.494 \text{ kJ}$

No. of moles of phenol burnt = $200 \times 10^{-3}/94 = 2.128\times10^{-3}$ mol

Thus, $\Delta_rU^o = -6.494 \text{ kJ}/(2.128 \times 10^{-3} \text{ mol}) = -3051.9 \text{ kJ mol}^{-1}$

$\Delta_rH^o = \Delta_rU^o + p\Delta_rV = \Delta_rU^o + \Delta_rn.R.T$

$= -3051900 \text{ J mol}^{-1} + ((6-7) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K})$

$= -3051900 - 2500 = -3054400 \text{ J mol}^{-1} = -3054.4 \text{ kJ mol}^{-1}$

Δ_rH^o = Sum for products of ($\nu \times \Delta_fH^o$) - Sum for reactants of ($\nu \times \Delta_fH^o$)

$= (6 \times -393.5 + 3 \times -285.8) - (\Delta_fH^o.(\text{phenol}) + 7 \times 0) = -3054.4 \text{ kJ mol}^{-1}$

$\Delta_fH^o.(\text{phenol}) = (6 \times -393.5 + 3 \times -285.8) + 3054.4 = -164.0 \text{ kJ mol}^{-1}$

May 2006. QUESTION 2

Explain briefly how and why the Gibbs free energy equation:

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

can be used to predict whether a constant temperature process is spontaneous, non-spontaneous or at equilibrium. [5]

For the reaction: $2CuO(s) \rightarrow Cu_2O(s) + 1/2\ O_2\ (g)$

Calculate ΔH^θ_{298}, ΔS^θ_{298}, ΔG^θ_{298} and the values of the equilibrium constant at this temperature and 1300 K, stating any assumptions you make. Use this information to assess if CuO(s) is stable at 298K and 1300K. [9]

What is the value of the equilibrium partial pressure of oxygen due to the above reaction at 1300K? [3]

At what temperature does the reaction become reversible? [3]

[$\Delta H^\theta_{f,298}(CuO)$ and $\Delta H^\theta_{f,298}(Cu_2O)$ are -152.7 and -167.3 kJ mol^{-1}, respectively. $S^\theta_{298}(CuO)$, $S^\theta_{298}(Cu_2O)$ and $S^\theta_{298}(O_2)$ are 42.6, 92.6 and 205.2 J $\text{mol}^{-1}\text{K}^{-1}$, respectively. R = 8.314 J $\text{mol}^{-1}\text{K}^{-1}$.]

Outline Answer:

For a process to be spontaneous, it must lead to an increase in the entropy of the universe. In chemistry, we usually consider changes taking place inside a closed isothermal system, and heat transferred to or from the surroundings causes changes in their entropy. At constant pressure the heat transferred is given by ΔH, and the change in entropy of the surroundings due to this transfer is thus -ΔH/T. This must be added to ΔS within the system to get the total entropy change of the universe. Hence this always has the opposite sign to that of ΔG for the process inside the system. So a spontaneous process must have a negative ΔG in the system, while a positive ΔG indicates a non-spontaneous process. A process at equilibrium will have ΔG of zero. The use of ΔG allows us to determine effects on the entropy of the universe by considering only changes within the system, which is very convenient for chemistry.

Reaction: $2CuO(s) \rightarrow Cu_2O(s) + 1/2\ O_2\ (g)$

$\Delta_r H^o$ = Sum for products of ($\nu \times \Delta_f H^o$) - Sum for reactants of ($\nu \times \Delta_f H^o$)

$= -167.3 + 0.5 \times 0 - (2 \times -152.7) = +138.1$ kJ mol^{-1} (at 298K)

$\Delta_r S^o$ = Sum for products of ($\nu \times S^o$) - Sum for reactants of ($\nu \times S^o$)

$= 92.6 + (0.5 \times 205.1) - (2 \times 42.6) = 110.0$ J mol^{-1}K^{-1} (at 298K)

$\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$

$\Delta_r G^o$ (298K) = 138100 J mol^{-1} - 298K × 110.0 J mol^{-1}K^{-1} = 105300 J mol^{-1}

= 105.3 kJ mol^{-1}

$\Delta_r G^\theta = -R.T.\ln K$

$$\ln K = \frac{-\Delta_r G^o}{R.T} = \frac{-105300 Jmol^{-1}}{8.314 Jmol^{-1}K^{-1} \times 298K} = -42.50$$

K = 3.48 × 10^{-19} (bar$^{0.5}$)

From the values of ΔG^θ and K, we can say the reaction is non-spontaneous and CuO is stable at 298K.

At 1300K, assuming that $\Delta_r H^\theta$ and $\Delta_r S^\theta$ are temperature independent.

$\Delta_r G^o$ (1300K) = 138100 J mol^{-1} - 1300K × 110.0 J mol^{-1}K^{-1} = -4900 J mol^{-1}

= -4.90 kJ mol^{-1}

$$\ln K = \frac{-\Delta_r G^o}{R.T} = \frac{+4900 Jmol^{-1}}{8.314 Jmol^{-1}K^{-1} \times 1300K} = 0.453$$

K = 1.574 (bar$^{0.5}$)

From the values of ΔG^θ and K, we can say the reaction is spontaneous and CuO is unstable at 1300 K.

$$K = \frac{a_{Cu_2O}.a_{O_2}^{0.5}}{a_{CuO}} = p_{O_2}^{0.5}$$

since the pure solid activities will be 1, and assuming ideal gas behaviour for O_2. Hence:
$p_{O2} = K^2 = 1.574^2 = 2.478$ bar.

The reaction becomes reversible (i.e. in equilibrium with 1 bar O_2) when $\Delta_r G^o = 0$, i.e. when $\Delta_r H^o = T.\Delta_r S^o$.
Thus we want $T = \Delta_r H^o/\Delta_r S^o = 138100\ \text{J mol}^{-1}/110.0\ \text{J mol}^{-1}\text{K}^{-1} = 1255\ \text{K}$
This assumes again that $\Delta_r H^o$ and $\Delta_r S^o$ are temperature independent.

August 2006 Question (1)

Use the Gibbs free energy equation and the Van't Hoff isotherm to derive the Van't Hoff reaction isochore: $\ln(K^o(T_1) = -\Delta H^o/R.T_1 + \Delta S^o/R$ [3]

The vapour pressure of n-hexane is 0.158 and 2.41 bar at 293 and 373 K, respectively. Use this information to determine the enthalpy, entropy and Gibbs free energy of vaporization at 333 K, stating any assumptions made. Comment on your entropy result with respect to Trouton's rule. [14]
Finally, use some or all of this information to determine the normal boiling point of n-hexane and comment on your result, given that the literature value is 69ºC. [3]

[$R = 8.314\ J\ mol^{-1}K^{-1}$]

Outline answer:
$\Delta G^o = \Delta H^o - T.\Delta S^o$ (Gibbs Free energy equation)
$\Delta G^o = -R.T.\ln K^o$ (Van't Hoff Isotherm)

If we assume ΔH^o and ΔS^o do not vary over the temperature range in question then, at T_1 (could have written just T and K):-
$-R.T_1.\ln K^o(T_1) = \Delta G^o\ (T_1) = \Delta H^o - T_1\Delta S^o$
Divide both sides by $-R.T_1$ to get
$\ln K^o(T_1) = -\Delta H^o/R.T_1.+\ \Delta S^o/R$, which is the van't Hoff isochore

In the example problem we may take K^o to be the vapour pressure of n-hexane (p_{vap}). With values at two different temperatures we can apply the van't Hoff isochore at each T to get 2 simultaneous equations and solve for $\Delta_{vap}H^o$ and $\Delta_{vap}S^o$. One route is to combine the simultaneous equations algebraically to get

$$\ln\frac{p_{vap,T1}}{p_{vap,T2}} = \frac{-\Delta_{vap}H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{0.158}{2.41} = -2.725 = \frac{-\Delta_{vap}H^o}{8.314 Jmol^{-1}K^{-1}}\left(\frac{1}{293K} - \frac{1}{373K}\right)$$

$\Delta_{vap}H^o = 2.725 \times 11358\ J\ mol^{-1} = 30948\ J\ mol^{-1} = 30.9\ kJ\ mol^{-1}$

Now from the original van't Hoff isochore we get
$\Delta_{vap}S^o/R = \ln(p_{vap}) +\ \Delta_{vap}H^o/R.T$
$\Delta_{vap}S^o = R.\ln(p_{vap}) +\ \Delta_{vap}H^o/T$
and apply at 293 K to get
$\Delta_{vap}S^o = 8.314\ J\ mol^{-1}K^{-1} \times \ln(0.158) + 30900\ J\ mol^{-1}/293K$
$= -15.3 + 105.6 = 90.3\ J\ mol^{-1}K^{-1}$

We have assumed that $\Delta_{vap}S^o$ and $\Delta_{vap}H^o$ are independent of temperature, so both will also be valid for 333 K. Hence at this temperature
$\Delta_{vap}G^o = \Delta_{vap}H^o - T.\Delta_{vap}S^o$
$= 30900\ J\ mol^{-1} - (333K \times 90.3\ J\ mol^{-1}K^{-1}) = 30900 - 30070 = 830\ J\ mol^{-1}$

Trouton's rule: For most non-polar liquids at their normal boiling points $\Delta_{vap}S$ is about 90 J $mol^{-1}K^{-1}$. This is because the entropy increase is primarily due to the increased degrees of freedom of the molecules in the gas phase. The calculated value for hexane, which is non-polar, is in good agreement with Trouton's rule.

At the normal boiling point
$\Delta_{vap}G^o = 0 = \Delta_{vap}H^o - T_b.\Delta_{vap}S^o$
$T_b. = \Delta_{vap}H^o/\Delta_{vap}S^o = 30900 \text{ J mol}^{-1}/90.3 \text{ J mol}^{-1}\text{K}^{-1} = 343 \text{ K}$
The calculated value for T_b is in good agreement with the literature value of 342 K implying that the underlying assumptions made were valid.

August 2006 Question 2
(a) Define the standard electrode potential of a redox couple. Use a sketch to highlight the main features of a standard hydrogen electrode and write out the associated electron transfer reaction. [6]

(b) Explain the function of the platinum metal in the Pt | Fe^{3+}, Fe^{2+} redox electrode.
If two half-cells consisting of the Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} are combined, the following equilibrium is reached: $Fe^{2+} + Ce^{4+} ==== Fe^{3+} + Ce^{3+}$
Sketch and label the likely appearance of such a cell. Given that the standard potentials at 25°C for the Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} redox couples are 0.770 V and 1.44 V, respectively, calculate the equilibrium constant, K , for the reaction. [8]
1
2(c) Corrosion is a process by which a metal is spontaneously oxidised in a solution. Calculate a value for ΔG for the corrosion of cadmium metal at 25°C under the conditions below and decide if the cadmium will corrode.
Cd | Cd^{2+} (10^{-6} mol dm^{-3}) || O_2 (1.6×10^4 Pa), H^+ (10^{-4} mol dm^{-3}) | Pt
with the cathodic reaction written as $O_2 + 4 H^+ + 4e^- \rightarrow 2 H_2O$ $E^o = 1.23$ V. [6]

[$F = 9.648\times10^4$ C mol^{-1}, $R = 8.314$ J $mol^{-1}K^{-1}$, E^o for $Cd/Cd^{2+} = -0.403$ V; 1 bar = 10^5 Pa]

Outline answer:
(a) The Standard electrode potential of a redox couple, or half cell, is the cell potential when connected to the standard hydrogen electrode acting as the anode, with all reagents at unit activity at 25°C.
The sketch of the standard H_2 electrode should show a platinum black indicator electrode immersed in 1M (or strictly unit activity) acid (usually HCl) with 1 bar of hydrogen being continuously bubbled through it. Half cell reaction is: $2 H^+ (aq) + 2e^- === H_2 (g)$

(b) In this half cell, the platinum acts as an indicator electrode, adopting a potential that reflects the levels of oxidised and reduced species, as defined by the Nernst equation. The diagram should show: one half cell with Fe^{3+} and Fe^{2+} in solution, and an indicator electrode, probably Pt; the second half cell with Ce^{4+} and Ce^{3+} in solution and its Pt electrode; an electrical connection between the electrodes via a voltmeter; a salt bridge connecting the electrolytes.

For the cell reaction written, Fe^{2+} is being oxidised, so this half cell is the anode.
$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 1.44 - 0.770 = 0.67$ V
$\Delta_r G^o = -n.F.E^o_{cell}$
$= -1 \times 9.648 \times 10^4 \text{ J V}^{-1}\text{mol}^{-1} \times 0.67 \text{ V} = -64640 \text{ J mol}^{-1} = -64.64 \text{ kJ mol}^{-1}$

$\Delta_r G^\theta = -R.T.\ln K$
$\ln K = -\Delta_r G^\theta/R.T = 64640 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}) = 26.09$
$K = 2.14\times10^{11}$

(c) Cell reaction is $2Cd + O_2 + 4 H^+ \leftrightarrow 2Cd^{2+} + 2 H_2O$
$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 1.23 - (-0.403) = 1.633$ V
The cell does not use standard conditions, so we need to calculate E_{cell} using the Nernst equation:
$E_{cell} = E^o_{cell} - (RT/nF)\ln Q$

$$Q = \frac{a^2_{Cd^{2+}}.a^2_{H_2O}}{a^2_{Cd}.a_{O_2}.a^4_{H^+}} \approx \frac{[Cd^{2+}]^2}{p_{O_2}.[H^+]^4} = \frac{(10^{-6})^2}{0.16\times(10^{-4})^4} = \frac{10^{-12}}{0.16\times10^{-16}} = 6.25\times10^4$$

Here we have taken the activity of solid Cd as 1, and also that of the solvent water (with these dilute solutions its activity is almost the same as pure water). For the activity of O_2 gas we have taken its pressure in bar, while we have assumed that the activity coefficients for Cd^{2+} and H^+ are close to 1 in dilute solutions.

$$E_{cell} = E^o_{cell} - \frac{R.T}{n.F}\ln Q = 1.633V - \frac{8.314 Jmol^{-1}K^{-1} \times 298K}{4\times9.648\times10^4 JV^{-1}mol^{-1}} \times 11.042 = 1.633 - 0.071 = 1.562V$$

$\Delta G = -n.F.E_{cell} = -4 \times 9.648 \times 10^4 \text{ J V}^{-1}\text{mol}^{-1} \times 1.562 \text{ V} = -603000 \text{ J mol}^{-1}$
$= -603 \text{ kJ mol}^{-1}$
This is big and negative – so the Cd will corrode.

May 2007, Question 2.

(a) Define the standard electrode potential of a redox couple. Use a sketch to highlight the main features of a standard hydrogen electrode and write out the associated electron transfer reaction. **[8]**

(b) Corrosion is a process by which a metal is spontaneously oxidised in a solution. The following cell can be used to assess the corrosion of tin by oxygen dissolved in water.
$Sn \mid Sn^{2+} (1 \text{ mol dm}^{-3}) \parallel O_2 (10^{-6} \text{ atm}), H^+ (10^{-7} \text{ mol dm}^{-3}) \mid Pt$
Sketch and label the likely appearance of this cell and explain briefly the role of the platinum electrode. Write out the overall redox reaction for the corrosion of tin by dissolved oxygen, given that the redox equation for oxygen is as follows:
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^0 = 1.230$ V. **[9]**

(c) Calculate the value of ΔG for the corrosion of tin metal at 25°C under the conditions in (b) and comment on the fact that in practice tin does not corrode in aqueous solution. **[8]**

[$F = 9.648\times10^4$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}, E^o (Sn/Sn^{2+}) = -0.136 V]

Outline answer:-
(a) See August 2006, Q2, above.

(b) The diagram should show: one half cell with a Sn metal electrode dipped in a 1 M Sn^{2+} solution; the second half cell with a Pt electrode, gas bubbled through with an O_2 partial pressure of 10^{-6} atm, and a 10^{-7} M solution of H^+; an electrical connection between the electrodes via a voltmeter; a salt bridge connecting the electrolytes. In the right hand half cell, the platinum acts as an indicator electrode, adopting a potential that reflects the interconversion of O_2, H^+ and H_2O, as defined by the Nernst equation.

The cell reaction (corrosion of Sn by dissolved O_2) is:

$$2Sn + O_2 + 4\,H^+ \leftrightarrow 2Sn^{2+} + 2\,H_2O$$

Could also write: $Sn + 0.5\,O_2 + 2\,H^+ \leftrightarrow Sn^{2+} + H_2O$

(c) $E^o_{cell} = E^o_{cathode} - E^o_{anode} = 1.230 - (-0.136) = 1.366$ V
The cell does not use standard conditions, so we need to calculate E_{cell} using the Nernst equation:
$E_{cell} = E^o_{cell}$ - (RT/nF)lnQ

$$Q = \frac{a^2_{Sn^{2+}}.a^2_{H_2O}}{a^2_{Sn}.a_{O_2}.a^4_{H^+}} \approx \frac{[Sn^{2+}]^2}{p_{O_2}.[H^+]^4} = \frac{1^2}{10^{-6}\times(10^{-7})^4} = \frac{1}{10^{-34}} = 10^{34}$$

Here we have taken the activity of solid Sn as 1, and also that of the solvent water (with these dilute solutions its activity is almost the same as pure water). For the activity of O_2 gas we have taken its pressure as given (strictly should be in bar, but since we are not given the conversion factor, actually 1.01325, we will just use the atm value – memorizing conversion factors is not expected). We have also assumed that the activity coefficient for H^+ is close to 1 in dilute solution, and in the absence of other information, that the activity coefficient for 1 M Sn^{2+} is also 1 – probably the least accurate assumption.

$$E_{cell} = E^o_{cell} - \frac{R.T}{n.F}\ln Q = 1.366V - \frac{8.314 Jmol^{-1}K^{-1}\times 298K}{4\times 9.648\times 10^4 JV^{-1}mol^{-1}}\times 78.288 = 1.366 - 0.503 = 0.863V$$

$\Delta G = -n.F.E_{cell} = -4 \times 9.648 \times 10^4$ J V^{-1}mol^{-1} $\times$ 0.863 V = -333000 J mol^{-1}
= -333 kJ mol^{-1}
This is big and negative – so the corrosion of Sn is spontaneous (thermodynamically favourable). The fact that is does not corrode must reflect kinetic barriers (i.e. it is extremely slow). Formation of an insoluble surface oxide layer may be one contribution.

May 2008, Q1

a) A bomb calorimeter has a heat capacity (calorimeter constant) of 1.374 kJ K^{-1}. Acetone (propanone, C_3H_6O (l), 210 mg) was burnt in the calorimeter, starting at 25.00 °C, and the temperature rise was 4.71K. Calculate ΔU^o and ΔH^o for combustion of acetone. [30%]

b) Explain the concept of a thermodynamic cycle in calculating changes in properties, making clear why these cycles work and how they are useful. [30%]

c) Estimate ΔH for the combustion of acetone at 273 K and 1 bar, making use of the following constant pressure heat capacities, all in J mol^{-1} K^{-1}: acetone (l), 124.7; O_2 (g), 29.36; H_2O (l), 75.29; CO_2 (g), 37.11. Make clear any assumptions you need to make. [40%]

Outline answer:

a) Relative molecular mass of acetone = $3 \times 12 + 6 + 16 = 58$
No. moles burnt = $210 \times 10^{-3}/58 = 3.621 \times 10^{-3}$
The total heat output was 1.374 kJ $K^{-1} \times 4.71$ K = 6.471 kJ
Hence heat evolved = $6.471/(3.621 \times 10^{-3}) = 1787$ kJ mol^{-1}
The calorimeter operates at constant volume, so no work is done, and hence
$\Delta U^o = -1787$ kJ mol^{-1}

Reaction is: C_3H_6O (l) + 4 O_2 (g) → 3 CO_2 (g) + 3 H_2O (l)
$\Delta_rH^o = \Delta_rU^o + p\Delta_rV = \Delta_rU^o + \Delta_rn.R.T$
$= -1787000 \text{ J mol}^{-1} + ((3-4) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K})$
$= -1787000 - 2500 = -1789500 \text{ J mol}^{-1} = -1789.5 \text{ kJ mol}^{-1}$
[Rounding to 4 sig figures equally if not more correct]

b) Thermodynamic cycles can be constructed for any thermodynamic function of state. If we go round a series of reactions or other processes such that we finally end up in exactly the same state as we started in, then any function of state cannot change as we go round the cycle. Hence the sum of changes in the individual reactions or processes must be zero. If we know the changes associated with all but one of the processes, we can calculate the change in the missing one. Often we can find a way to go between a starting and end state of interest via a roundabout route, but where the changes in properties for each step are either known or can be easily estimated. Hence we calculate the value we want for the direct change.

c) We could go between the same starting and final states as follows: 1) heat acetone and O_2 at constant pressure from 273 to 298 K; 2) carry out reaction at 298 K, with Δ_rH^o as calculated above; 3) cool the CO_2 and H_2O from 298 to 273K. The sum of these three must have the same ΔH as the direct combustion reaction at 273 K. To work out the ΔH for steps 1 and 3 we use the heat capacities given, which we have to assume are independent of temperature in the range 273 to 298 K (reasonably accurate). We also have to assume that the product is H_2O (l) – if it was H_2O (s) we would need to add in an extra latent heat term.

Heating, step 1: $\Delta H = 25 \text{ K} \times (124.7 \text{ J mol}^{-1} \text{ K}^{-1} + 4 \times 29.36 \text{ J mol}^{-1} \text{ K}^{-1})$
$= +6054 \text{ J mol}^{-1}$

(NB, for each mole of acetone or reaction we need to heat 4 mol O_2)
Cooling, step 3: $\Delta H = -25\ K \times (3 \times 75.29\ J\ mol^{-1}\ K^{-1} + 3 \times 37.11\ J\ mol^{-1}\ K^{-1})$
$= -8430\ J\ mol^{-1}$
Hence for the combustion at 273 K we estimate
$\Delta_r H = -1789500 + 6054 - 8430\ J\ mol^{-1} = -1792000\ J\ mol^{-1} = -1792\ kJ\ mol^{-1}$

May 2008, QUESTION 2

The following electrochemical cell has been studied:

Pt|O_2(g, 1 bar)|HCl (aq, pH 0)||$AgNO_3$ (0.1 M)|Ag $\qquad E_{cell} = -0.497$ V at 25 °C

$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O \qquad E^o = 1.229$ V
$Ag^+ + e^- \rightarrow Ag \qquad E^o = 0.800$ V

a) Write out the cell reaction, and calculate E^o_{cell}. [20%]
b) Draw a diagram showing the essential features of this cell. [20%]
c) Explain how an electrochemical cell can be used to measure the activity coefficients of ions in solution, stating the equation that relates E_{cell} and E^o_{cell}. [25%]
d) Estimate the activity and activity coefficient of Ag^+ in 0.1 M $AgNO_3$ (assume that pH 0 means that the activity of H^+ is 1). [35%]

Answer outline:-
a) $2\,H_2O + 4Ag^+\,(aq) \rightarrow O_2\,(g) + 4\,H^+\,(aq) + 4Ag\,(s)$
Also acceptable to have other multiples e.g.
$H_2O + 2Ag^+\,(aq) \rightarrow 0.5\,O_2\,(g) + 2\,H^+\,(aq) + 2Ag\,(s)$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.800 - 1.229 = -0.429$ V

b) The diagram should show: one half cell with aqueous HCl solution, a Pt electrode, and O_2 gas bubbled over it; the second half cell with Ag^+ in solution and an Ag electrode; an electrical connection between the electrodes via a voltmeter; a salt bridge connecting the electrolytes.

c) $E_{cell} = E^o_{cell} - (RT/nF)\ln Q$
If we know the standard potentials (i.e. E^o_{cell}) and we measure the cell potential under non-standard conditions, we can use this equation to calculate Q for those conditions. Q is the ratio of the activities of all species involved in the cell reaction. If all but one of these are known (e.g. by definition for solids, from pressure for gases), the remaining one can be calculated from the known value of Q. Assuming we know the molar concentration of the ion whose activity we have calculated, we obtain its activity coefficient. (The issue of single ion activities being in principle unmeasurable is beyond

the scope of the class, but credit will be given to any student who mentions it from further reading.)

d) For the cell reaction in this case we re-arrange the equation above to get
$\ln Q = (nF/RT)(E^o_{cell} - E_{cell})$
then substitute to get

$$\ln Q = \frac{4 \times 9.648 \times 10^4\, JV^{-1}mol^{-1}}{8.314 Jmol^{-1}K^{-1} \times 298K} \times (-0.429V - -0.497V) = 155.8V^{-1} \times 0.068V = 10.59$$

Hence $Q = 3.982 \times 10^4$
For this cell reaction

$$Q = \frac{a_{O_2}.a^4_{H^+}a^4_{Ag}.}{.a^2_{H_2O}.a^4_{Ag^+}} \approx \frac{1 \times 1^4 \times 1^4}{1^2 \times a^4_{Ag^+}}$$

Here we have taken all but one of the activities as equal to 1: of O_2 gas at 1 bar pressure, of H^+ as told in the question, of pure solid Ag (standard state), and of the solvent water (in dilute solution its activity is almost the same as pure water).

Hence $(a_{Ag}+)^4 \approx 1/Q = 2.512 \times 10^{-5}$
and $a_{Ag}+ = 0.0708$
We know that its concentration = 0.1 M, hence its activity coefficient is 0.708.