1. When heated to about 300 °C, zirconium oxide (ZrO_2) becomes a solid electrolyte due to mobile O^{2-} ions. The mobility of the O^{2-} ions is increased by doping ZrO_2 with small amounts of CaO, introducing "holes" (missing O^{2-} ions) in the crystal lattice into which O^{2-} ions can diffuse.

Zirconium oxide solid electrolytes are widely used as electrochemical sensors to monitor oxygen levels during the operation of internal combustion engines. Obtaining the correct air:fuel ratio is important to maximize engine performance and to reduce the emission of pollutants.

A schematic diagram of the zirconium oxide cell

$$Pt(s)\ |\ O_2(g, 0.20 \text{ bar in air})\ |\ ZrO_2(s)\ |\ O_2(g, p_{O2?})\ |\ Pt(s)$$

is shown below. One side of the zirconium oxide electrolyte is exposed to air, providing a reference oxygen pressure at approximately 0.20 bar. The other side of the electrolyte in contact with the engine exhaust. Porous platinum serves as the electrodes.
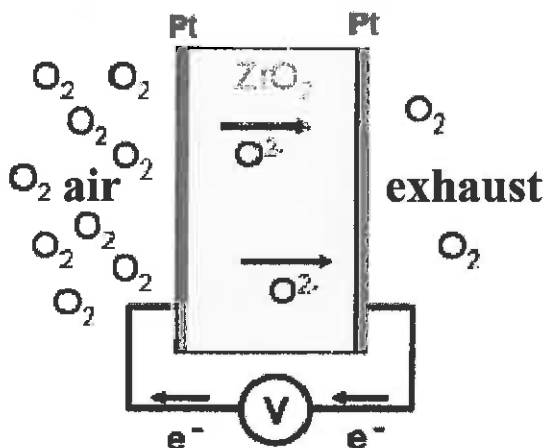
a) Write the anode reaction, cathode reaction, the overall cell reaction and the Nernst equation for the cell.

b) Calculate the cell voltage for an engine with a "lean" air:fuel mixture (too much air) that gives $p_{O2} = 0.05$ bar in exhaust at 300 °C.

c) Calculate the cell voltage for an engine with a "rich" air:fuel mixture (too much fuel) that gives $p_{O2} = 10^{-5}$ bar in exhaust at 300 °C.

d) Why is platinum used for the electrodes?

e) Why are the electrodes porous?

2. The potentials of electrochemical concentration cells, such as ZrO_2 oxygen sensors and pH cells, depend logarithmically on the concentration of the detected species. The logarithmic relation has important consequences for the precision of electrochemical concentration measurements.

Suppose a ±0.002 volt error is made in the measurement of potential of the pH cell

$$Ag(s)\,|\,AgCl(s)\,|\,Cl^-(aq), H^+(aq, pH_{ref} = 7.00)\,||\,Cl^-(aq), H^+(aq, a_{H+})\,|\,AgCl(s)\,|\,Ag(s)$$
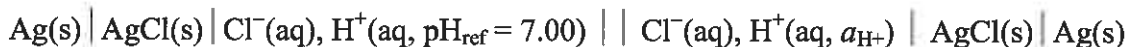
For each of the following cell potentials, calculate the corresponding errors in the calculated hydrogen molality (use $\gamma_{H+} = 1$) at 25 °C.

E/volt:	−0.355	−0.237	−0.118	0.296

Assume errors in the temperature and reference pH are negligible.

3. This question compares the thermodynamics of a direct chemical reaction with the thermodynamics of the same reaction in an electrochemical cell. Significantly different amounts of work are obtained depending on how the reaction is carried out.

Plan A (Direct Chemical Reaction)

a) Calculate q, w, ΔU, ΔH and ΔG for the following reaction at 25 °C and 1 bar. Are q and ΔH identical? *Data:* $\Delta H_{fm}°(H_2O, l) = -285.8$ kJ mol^{-1} $\Delta G_{fm}°(H_2O, l) = -237.1$ kJ mol^{-1}

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l)$$
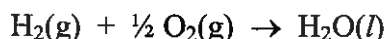
b) Suppose the heat from the reaction is used to run a heat engine operating between 500 K (the hot reservoir at T_H) and 300 K (the cold reservoir at T_C). Use the Carnot relation

$$\varepsilon = 1 - (T_C/T_H)$$

for the efficiency of a reversible heat engine to calculate the maximum amount of work that can be done on the surroundings.

Plan B (Electrochemical Reaction)

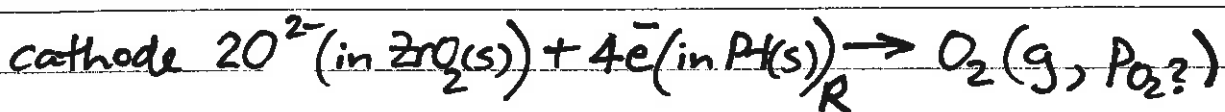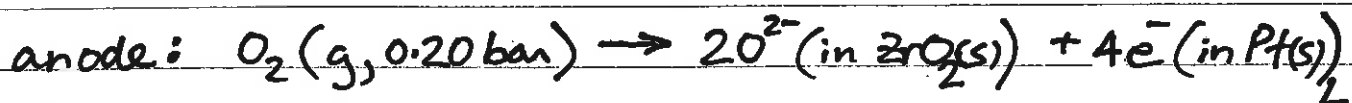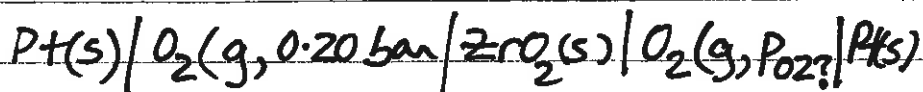a) Calculate q, w, ΔU, ΔH and ΔG for the following reaction at 25 °C and 1 bar

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l)$$
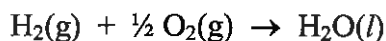
carried out in the fuel cell $Pt(s)\,|\,H_2(g, 1bar)\,|\,KOH(aq)\,||\,KOH(aq)\,|\,O_2(g, 1 bar)\,|\,Pt(s)$.

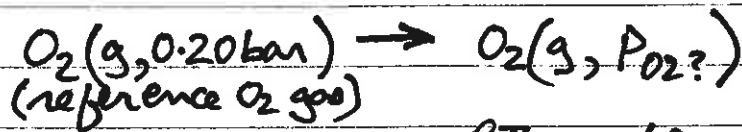b) Are q and ΔH identical? Explain.

c) Compare the amount of work that can be done on the surroundings using plan A and plan B. This result is one of motivations for fuel cell research and development in many laboratories.

Chem 232   Tutorial #3

(Q1) a) ZrO_2 solid electrolyte oxygen sensor

cell: $Pt(s) \mid O_2(g, 0.20 \, bar \mid ZrO_2(s) \mid O_2(g, P_{O2}?) \mid Pt(s)$

anode: $O_2(g, 0.20 \, bar) \longrightarrow 2O^{2-}(in \, ZrO_2(s)) + 4\bar{e}(in \, Pt(s))_L$

cathode $2O^{2-}(in \, ZrO_2(s)) + 4\bar{e}(in \, Pt(s)) \underset{R}{\longrightarrow} O_2(g, P_{O2}?)$

overall: $O_2(g, 0.20 \, bar) \longrightarrow O_2(g, P_{O2}?)$
                    (reference O_2 gas)

Nernst equation $(n=4)$: $E = -\dfrac{RT}{4F} \ln \left(\dfrac{P_{O2}?}{P_{O2 \, ref}} \right)$

(No E°! This is a concentration cell.)

$P_{O2 \, ref} = 0.20 \, bar$ using $O_2(g)$ in air

b)   lean air:fuel mixture $P_{O2}? = 0.05 \, bar$

$E = -\dfrac{RT}{4F} \ln \dfrac{0.05}{0.20}$

$= -\dfrac{(8.314 \, J \, K^{-1} mol^{-1})(573 \, K)}{4(96485 \, C \, mol^{-1})} \ln \left(\dfrac{0.05}{0.20} \right)$
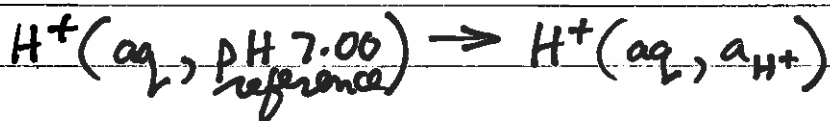
$E = 0.0171 \, volt$

(Q1 cont.)

c)   rich air:fuel mixture $P_{O_2}? = 10^{-5}$ bar

$$E = -\frac{RT}{4F} \ln\left(\frac{10^{-5}}{0.20}\right) = 0.122 \text{ volt}$$

d)   Pt electrodes are chemically inert and can "survive" for years in hot, reactive engine exhaust gases

e)   The Pt electrodes are porous to allow O_2 gas to enter the solid ZrO_2 electrolyte.

(Q2)   another concentration cell, overall:

$$H^+\left(aq., \underset{\text{reference}}{pH\ 7.00}\right) \rightarrow H^+\left(aq., a_{H^+}\right)$$

Nernst equation $E = -\frac{RT}{F} \ln\left(\frac{a_{H^+}}{a_{H^+,\text{ref}}}\right)$

for the error analysis, assume ideal solutions:

Left $a_{H^+,\text{ref}} = \left(\gamma_{H^+} m_{H^+}\right)_{\text{ref}} = 10^{-7.00} \approx m_{H^+,\text{ref}}$

Right $a_{H^+} \approx m_{H^+}$

$$E = -\frac{RT}{F} \ln\left(\frac{m_{H^+}}{10^{-7.00}}\right)$$

(Q2 cont.)

$$m_{H+} = m_{H+ref}\, e^{-FE/RT}$$

$F = 96485\ C\,mol^{-1}$
$T = 298\ K$
$R = 8.314\ J\,K^{-1}mol^{-1}$

E / volt	m_{H+} / $\frac{mol}{kg}$	error in m_{H+} (8% of m_{H+})
-0.355	0.100	0.008
-0.237	0.00101	0.00008
-0.118	1.16×10^{-6}	0.09×10^{-6}
0.296	9.91×10^{-13}	0.8×10^{-3}

$$\frac{dm_{H+}}{dE} = -m_{H+ref}\,\frac{F}{RT}\,e^{-FE/RT} = -m_{H+}\,\frac{F}{RT}$$

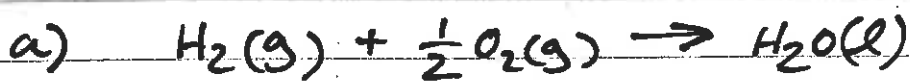$$\frac{dm_{H+}}{m_{H+}} = -\frac{F}{RT}\,dE$$

$$\frac{\text{error in } m_{H+}}{m_{H+}} = -\frac{F}{RT}\,(\text{error in } E)$$

$$= -\frac{96485}{8.314(298)}\,0.002$$

$$= -0.08$$

a 0.002 volt error in E produces an 8% error in m_{H+}
(significant)

(Q3) Plan A

a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

$\Delta H = \Delta H_{fm}^°(H_2O, l) - \Delta H_{fm}^°(H_2, g) - \frac{1}{2}\Delta H_{fm}^°(O_2, g)$

$= -285.8 - 0 - 0 = -285.8 \text{ kJ mol}^{-1}$

$\Delta H = q$ (constant pressure, only pV work)

$$
\begin{array}{ll}
\text{why?} & dH_p = d(U + pV)_p \\
& = dU + d(pV)_p \\
& = dq + dw + pdV + V\cancelto{0}{dp} \\
& = dq - pdV + pdV \quad (\text{only pV work}) \\
& = dq
\end{array}
$$

$\Delta G = \Delta G_{fm}^°(H_2O, l) - \Delta G_{fm}^°(H_2, g) - \frac{1}{2}\Delta G_{fm}^°(O_2, g)$

$= -237.1 - 0 - 0 = -237.1 \text{ kJ mol}^{-1}$

$w = -\int P_{ext} \, dV = -p\int dV \quad$ const. pressure
$\phantom{w = -\int P_{ext}}_{\text{negligible}} \quad$ ideal gases $V_m = V/n = RT/p$

$= -p\left(V_m(H_2O, l) - V_m(H_2, g) - \frac{1}{2}V_m(O_2, g)\right)$

$= p\left[\dfrac{RT}{p} + \dfrac{1}{2}\dfrac{RT}{p}\right]$

$= \dfrac{3}{2}RT = \dfrac{3}{2}\left(8.314 \dfrac{J}{K \, mol}\right)(298.15 K)$

$w = 3.72 \text{ kJ}$ $\qquad \Delta U = q + w = -285.8 + 3.72$

$\qquad\qquad\qquad\qquad \Delta U = -282.1 \text{ kJ}$

(Q3 cont.)

b) ideal engine efficiency $\varepsilon = 1 - \dfrac{T_c}{T_H}$

$\varepsilon = 1 - \dfrac{300\,K}{500\,K} = 0.400$ (40% efficient)

40% of the heat from the reaction can be converted to work done on the surroundings

$$\begin{array}{l}\text{work done} \\ \text{(at best)}\end{array} = 0.400\,|\Delta H|$$

$$= 0.400\,(285.8\,kJ)$$
$$= 114.3\,kJ$$

Plan B (Electrochemical Reaction)

$\Delta H = -285.8\,kJ\,mol^{-1}$
$\Delta G = -237.1\,kJ\,mol^{-1}$
$\Delta U = -282.1\,kJ\,mol^{-1}$

} same as for Plan A!
why? ΔH, ΔG and ΔU
are state functions
(path-independent)

What's different?   w and q

for the electrochemical cell (assumed reversible)

w_e = electrical work $= \Delta G = -237.1\,kJ\,mol^{-1}$

*** important ***   237.1 kJ of electrical work
(part c)   can be done on the surroundings
(This is more than twice as much
work done by the heat engine
using the same reaction)
(Plan A)

(Q3 cont.)

$$\text{total work} = w_e + w_{pv}$$

$$w = (-237.1 + 3.7) \text{ kJ mol}^{-1}$$

$$w = -233.4 \text{ kJ mol}^{-1}$$

$$q = \Delta U - w = -282.1 - (-233.4)$$
$$q = -48.7 \text{ kJ mol}^{-1}$$

notice $q \neq \Delta H = -285.8 \text{ kJ mol}^{-1}$

Why?

$$dH_p = d(U + pV)_p$$

$$= dU + pdV + \cancel{Vdp}^{\,0}$$

$$= dq + dw + pdV$$

for the cell,
two kinds
of work

$$dw = dw_e + dw_{pv}$$

$$dH_p = dq + dw_e - pdV + pdV$$

$$\Delta H = q + w_e$$

Summary:

	Plan A	Plan B
$\Delta H / \text{kJ mol}^{-1}$	-285.8	-285.8
$\Delta G / \text{kJ mol}^{-1}$	-237.1	-237.1
$\Delta U / \text{kJ mol}^{-1}$	-282.1	-282.1
q	-285.8	-48.7
w	3.7	-233.4