**PRINT**

FIRST NAME _____    LAST NAME    _____

STUDENT NUMBER  _____

UNIVERSITY OF TORONTO

FINAL EXAM, APRIL 14, 2000

CHE 150F - CHEMISTRY

EXAMINERS - M.T. Kortschot, W.H. Burgess

1.  Do all questions. The marking scheme for each question is indicated in the margin.  The marks add up to 100.

2.  Calculator Type 2 - Non-programmable calculators are allowed. No programmable calculators are allowed.   No other aids are allowed.

3.  **ALL WORK IS TO BE DONE ON THESE SHEETS!** Use the back of the page if you need more space. Be sure to indicate clearly if your work continues elsewhere. **DO NOT SEPARATE THE SHEETS EXCEPT FOR PAGE 8 WHICH IS BLANK AND MAY BE SEPARATED AND USED AS SCRAP.   PAGE 8 WILL NOT BE MARKED.  ALWAYS PUT YOUR FINAL ANSWERS IN THE BOXES PROVIDED.**

Equations that may be of some use.

$$dU = TdS - PdV$$

$$H = U + PV$$

$$G = H - TS$$

$$\Delta G = \Delta G^o + RT \ln Q$$

$$\Delta G^o = -RT \ln K$$

$$\ln\left(\frac{P_{vap2}}{P_{vap1}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$R = 8.314\, J/(mol\,K)$$

$$1atm = 101.3 kPa = 760 mmHg$$

$$273.15 K = 0°C\quad 1m^3 = 1000L$$

Molar Masses (g/mol)
H = 1.01, C = 12.01,  O = 16.00, S = 32.06

Marks

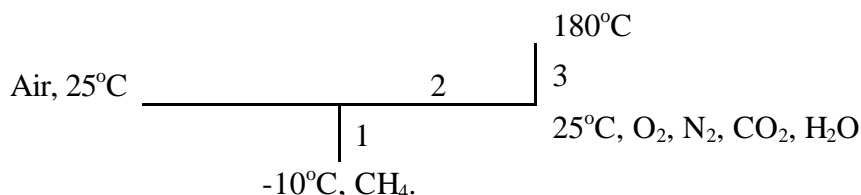| | |
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| 1 | |
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| TOTAL | |

## Problem 1 [15 marks total]

An industrial furnace burns methane ($CH_4$) with a 40% excess of air to $CO_2$ and $H_2O$. The methane undergoes an expansion prior to combustion, which gives it a starting temperature of – $10.0^oC$. The methane is mixed in the furnace with air that is initially at $25^oC$ and has a composition of 79 mol% $N_2$ and 21 mol% $O_2$. After passing through a heat exchanger, the exhaust gases leave at $180^oC$. You may assume that all gases are ideal, and that the pressure is constant at 1.0 atm.

a) How much energy is recovered by the heat exchanger for each mole of methane burned?
b) What is the volume of product gases (at $180^oC$, 1.0 atm) per mole of methane burned?

|  | $\Delta H_f^o$ (kJ/mol) | $C_P^o$ (J/mol K) |
|---|---|---|
| $CH_4$ (g) | -74.8 | 35.3 |
| $O_2$ (g) | 0 | 29.4 |
| $N_2$ (g) | 0 | 29.1 |
| $CO_2$ (g) | -393.5 | 37.1 |
| $H_2O$ (g) | -241.8 | 33.6 |

ANSWERS:     a) q = 734   kJ             b) V = 533  L

a) basis 1 mol $CH_4$.     $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$180^oC$

Air, $25^oC$ ———————————— 2 | 3

| 1     $25^oC$, $O_2$, $N_2$, $CO_2$, $H_2O$

$-10^oC$, $CH_4$.

| Product gas | $O_2$ | $N_2$ | $CO_2$ | $H_2O$ |  |
|---|---|---|---|---|---|
| n | 0.8 | 10.53 | 1.0 | 2.0 | =14.33 mol |

$\Delta H_1 = $  35 x (35.3/1000) = 1.24 kJ
$\Delta H_2 = [(-393.5) + 2$ x $(-241.8)] – ( - 74.8) = -802.3$ kJ
$\Delta H_3 = (0.8$ x $29.4 + 10.53$ x $29.1 + 37.1 + 2$ x $33.6)$ x $155/1000 = 67.3$ kJ
$\Delta H = 1.24 + (-802.3) + 67.3 = 733.8$ kJ $= $~$734$ kJ

b) V = (14.33 x 8.314 x 453.2)/101.3 = 533 L

## Problem 2 [15 marks total]

A gas stream at 900K and 2.00 atm has the following composition: CO 30.0 mol%, $CO_2$ 70 mol%.

a) Using appropriate calculations, show that carbon deposits have a tendency to form as a result of the reaction $2CO\ (g) \Leftrightarrow C$ (graphite) $+ CO_2\ (g)$.

b) This tendency can be eliminated by reducing the total pressure **or** increasing the temperature.

    i)       Determine the pressure just below which carbon deposits will not form. Assume that that the temperature and composition of the stream remain unchanged.

    ii)      Determine the temperature just above which carbon deposits will not form. Assume that the pressure and composition of the stream remain unchanged.

| Data at 900K: | $\Delta H_f^o$ (kJ/mol) | $\Delta G_f^o$ (kJ/mol) |
|---|---|---|
| C (graphite) | 0 | 0 |
| CO (g) | -111.46 | -191.71 |
| $CO_2$ (g) | -394.43 | -395.72 |

ANSWERS:   b) i)  P = 1.50  atm           ii) T = 911  K

a)  $2CO \Leftrightarrow C_{graphite} + CO_2$.    $\Delta G_R^o = (-395.72) - (-2 \times 191.71) = -12.30$ kJ

    $Q_P = n_{CO2}n_T/n^2_{CO}P = (0.7 \times 1)/(0.3^2 \times 2) = 3.89$ atm$^{-1}$.

    $\Delta G = \Delta G^o_R + RT\ ln\ Q_P = -12300 + 8.314 \times 900 \times ln\ 3.89 = -2136$ J

    Hence graphite deposits tend to form.

b)i) $K_P = e^{-\Delta G_R^o /(RT)} = e^{12300/(8.314 \times 900)} = 5.17$ atm$^{-1}$.

    $5.17 = (0.7 \times 1)/(0.3^2 P)$,    $P = 1.504 = \sim 1.50$ atm

  ii) $K_p = 3.89$ atm$^{-1}$.    $\Delta H_R^o = (-394.43) - (-2 \times 111.46) = -171.51$ kJ

    $\Delta S^o = (\Delta H^o - \Delta G^o)/T = [(175100) - (-12300)]/900 = -176.9$ J/K

    $\Delta G_T^o = \Delta H^o_{900} - T\Delta S^o_{900}$.

    $-8.314 \times T \times ln\ 3.89 = -171510 + T \times 176.9$,      $T = 911.3 = \sim 911$ K

## Problem 3 [15 marks total]

Data: vapour pressures at 30°C: benzene 119 mmHg; toluene 36.7 mmHg.

100 moles of a gaseous mixture of nitrogen, benzene and toluene were cooled from 120°C to 30°C at a constant pressure of 1.0 atm. As a result of the cooling, some of the benzene and toluene condensed. Before cooling the gaseous mixture was 45.0mol% nitrogen and after cooling it was 90.0 mol% nitrogen. Calculate:
a) the total number of moles of condensate
b) the number of moles of toluene in the condensate.

ANSWER:   (a) 50.0 mol                              (b) 26.1 mol

a)  $n_c^v/n_{N2} = P_c / P_{N2}$,   $n_c^v = n_{N2}P_c / P_{N2} = 45.0 \times (0.1/0.9) = 5.0$ mol
    $n_c^1 = 55.0 - 5.0 = 50.0$ mol of condensate

b)  $P_c = PY_c = 760 \times 0.1 = 76.0$ mm Hg
    $76.0 = P^*_b X_b + P^*_t X_t = 119 \times (1 - X_t) + 36.7 X_t$.
    $X_t = 0.522$  $n_t^1 = 50 \times 0.522 = 26.1$ mol

## Problem 4 [10 marks total]

A gaseous mixture entering a continuous flow reactor operating at steady state has the following composition in mol%: $N_2$ 31.0, $H_2$ 69.0. In the reactor some of the $N_2$ and $H_2$ combine to form $NH_3$. The gaseous mixture leaving the reactor is 46.2 mol% $H_2$. Calculate:
a) the moles of $NH_3$ produced per 100 moles of entering gas,
b) the percent yield of $NH_3$.

| ANSWERS: | a) $n_{NH3}$ = 22.0 mol | b) % yield = | 47.8 % |
|---|---|---|---|

a) $N_2 + 3H_2 \rightarrow 2NH_3$.                    100 mol basis

|  | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| I | 31.0 | 69.0 | 0 |
| C | - x | - 3x | 2x |
| F (tot =100-2x) | 31.0 - x | 69.0 – 3x | 2x |

$(69.0 – 3x)/(100 – 2x) = 0.462$,     $x = 11.0$mol,     $n_{NH3}$ = 2 x 11.0 = 22.0 mol

b)  % yield = [(actual)/(theoretical max)] x 100%.
    $H_2$ is the limiting reagent, so theoretical max = (2/3) x 69.0 = 46.0
    % yield = 22.0/46.0 x 100% = 47.8%

## Problem 5 [10 marks total]          Data: MM of $H_2SO_4$ = 98.08 g/mol, $H_2O$ = 18.02 g/mol

a)  A compound $A_2B$ is 36.35 % by mass B. Determine the percent by mass of B in the compound $A_2B_5$.
b)  A solution is 15.00 mol % $H_2SO_4$ and at 20°C has a density of 1.3854 g/ml. Calculate:
    i)        The molality of the $H_2SO_4$,
    ii)       The molarity of the $H_2SO_4$ at 20°C.

| ANSWERS: | a) %B = 74.06 % | b) i) $m$ = 9.793 mol/kg, | ii) M = 6.920 mol/L |
|---|---|---|---|

a)  Let mass of A = 1 in arbitrary mass units. 2/(2 + B) = 0.6365, B = 1.422 in AU
    (5 x 1.422)/(5 x 1.422 + 2) x 100% = 74.06%

b)  basis 100 mol
 i) m = 15.00/[85.00 x (18.02/1000)] = 9.793 mol/kg
 ii) M = 15.00/[(15.00 x 85.00 + 85.00 x 18.02)/1385.4] = 6.920 mol/L

## Problem 6 [20 marks total]

Data for $N_2$  $C_p = 29.1$ J/molK

Data for $H_2O$: $C_p$ (l) = 75.3 J/mol K, $C_p$ (g) = 33.6 J/mol K, $\Delta H^o_{vap}(100^o\,C) = 40.65 kJ\,/\,mol$
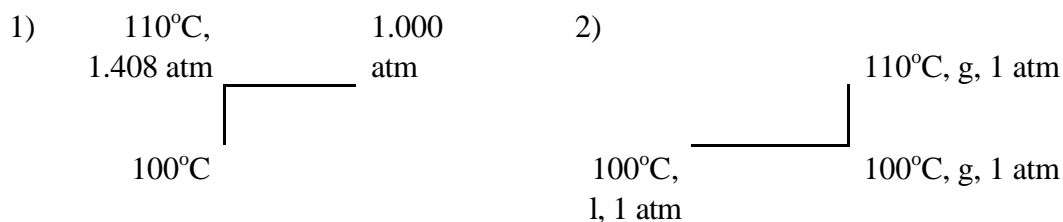
*The change in enthalpy and entropy of a liquid with pressure may be neglected.*

a) Calculate the vapour pressure of water at 110°C.
b) Calculate entropy twice using two separate paths for the process

$$H_2O \text{ (liquid, 100°C, 1.0 atm)} \Rightarrow H_2O \text{ (gas, 110°C, 1.0 atm)}$$

and thus demonstrate that entropy is a state function.

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ANSWERS:     a) $P_{vap} = 1.408$ atm          b) $\Delta S_{sys} = 109.84$ J/molK

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a) $ln\,(P*_2/P*_1) = -(\Delta H_v/R)[(1/T_2) - (1/T_1)]$

$ln\,(P*_2/1) = -(40650/8.314)[(1/383.15) - (1/373.15)]$,     $P*_2 = e^{0.3149} = 1.408$ atm

b)

1)        110°C,                1.000              2)

1.408 atm               atm                                                  110°C, g, 1 atm

100°C                                      100°C,          100°C, g, 1 atm

l, 1 atm

1) $\Delta H_v(110°C) = -10 \times 75.3 + 40650 + 10 \times 33.6 = 40233$ J/mol

$\Delta S = 75.3 \times ln\,(383.15/373.15) + (40233/383.15) + [-8.314\,ln(1/1.408)] = 109.84$ J/molK

2) $\Delta S = (40650/373.15) + 33.6\,ln\,(383.15/373.15) = 109.83$ J/molK

c) One mole of nitrogen at 25°C and 1.0 atm pressure is allowed to expand into a **vacuum** to a final volume of double its original volume.  If the process takes place inside an adiabatic container, and the nitrogen behaves as an ideal gas, what is the final temperature T?  Justify your answer.

d) For the process described in part c) compute the change in entropy of the system, the surroundings, and the universe.

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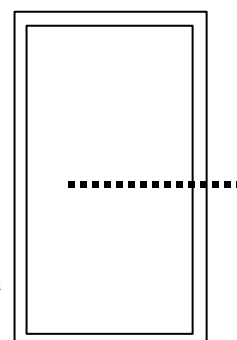
ANSWERS: c) T =   289 K  d) $\Delta S_{sys} = 5.76$  J/molK     $\Delta S_{surr} =$   0 J/molK $\Delta S_{univ} = 5.76$ /molK

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c) $\Delta U = q + W$,         for an ideal gas $C_v\Delta T = q + W$

since q & W = 0 then $\Delta U = 0$ so $\Delta T = 0$

d)$\Delta S_{system} = - R\,ln\,(P_2/P_1) = - R\,ln\,(V_1/V_2) = -8.314\,ln\,(1/2) = 5.76$ J/molK

$\Delta S_{surr} = 0$,        $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surr} = 5.76$ J/molK

### Problem 7 [15 marks total]

a) Starting from the definitions of $H$, $G$, and the expression $dU = TdS - PdV$, derive an expression for $dG$.

b) If $z$ is expressed as a function of $x$ and $y$, write an expression for $dz$ in terms of partial derivatives. Repeat for $G$ as a function of $P$ and $T$.

c) Write the Maxwell relationship resulting from the comparison of the answers to a) and b).

d) At constant $T$ changes in $S$ may be written as $dS = \left(\dfrac{\partial S}{\partial P}\right)_T dP$. Using the Maxwell relationship of part c), find $\boldsymbol{D}S$ for a pressure change from $P_1$ to $P_2$ at constant $T$ for one mole of a gas obeying the truncated van der Waals equation of state:

$$PV = RT + P\left(b - \frac{a}{RT}\right)$$

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ANSWERS:　(a) $dG = VdP - SdT$

(b) $dz = (\partial z/\partial x)_y dx + (\partial z/\partial y)_x dy$　　$dG = (\partial G/\partial P)_T dP + (\partial G/\partial T)_P dT$

(c) $(\partial V/\partial T)_P = - (\partial S/\partial P)_T$　　　(d) $\boldsymbol{D}S = -R\ \ln(P_2/P_1) - (a/RT^2)(P_2 - P_1)$

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a) $H = U + PV$　　　　$dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$

$G = H - TS$,　　　　$dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$

b) $z = f(x,y)$,　　$dz = (\partial z/\partial x)_y dx + (\partial z/\partial y)_x dy$　　$dG = (\partial G/\partial P)_T dP + (\partial G/\partial T)_P dT$

c) Since the order of differentiation is immaterial
$$\left[\frac{\partial\left(\dfrac{\partial z}{\partial x}\right)_y}{\partial y}\right]_x = \left[\frac{\partial\left(\dfrac{\partial z}{\partial y}\right)_x}{\partial x}\right]_y$$

Since $dG = VdP - SdT$ is an exact differential, we can write $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$.

d) $V = (RT/P) + b - (a/RT)$

$(\partial V/\partial T)_P = (R/P) + (a/RT^2)$　　　and　　　$(\partial S/\partial P)_T = -(R/P) - (a/RT^2)$

$$\Delta S = \int_{P_1}^{P_2}\left(\frac{\partial S}{\partial P}\right)_T dP = -R\ \ln(P_2/P_1) - (a/RT^2)(P_2 - P_1)$$