Name: Student Number:

CHM 2131
Midterm Test, October 23rd 2015

This is a closed book exam with no notes allowed.
Calculators are permitted.

Write all the formulas that you use to solve the questions and show all your work.

Remember to include units in all your calculations**.** Marks will be deducted if units are not shown.

Data section and equation sheet available at the end of the exam.

Please note that when re-marking,
I will look at the full exam.

Maximum score = 62 / 60

Q1 ______________/10

Q2 ______________/6

Q3 ______________/16

Q4 ______________/4

Q5 ______________/10

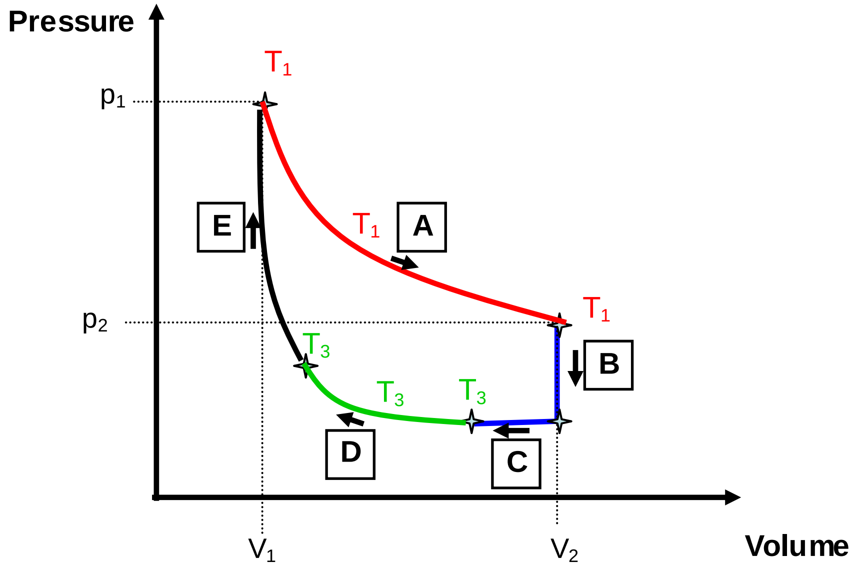
Q6 ______________/5

Q7 ______________/5

Q8 ______________/6

Total ______________/ 60

1. (10 points) For an ideal gas undergoing the following processes labelled A, B, C, and D in the graph, **write ALL that apply** from the list on the right (multiple matches may be possible).

<table>
<tr><th>Processes</th><th>Many of these apply to more than one process.</th></tr>
<tr><td>
</td><td>1. adiabatic process
2. isothermal expansion
3. w=0
4. q=0
5. $\Delta U=0$
6. w=-q
7. work is positive (done on the system)
8. $w = -\int_{V_i}^{V_f} p\,dV$
9. $w = -p_{ext}\Delta V$
10. $\Delta H = C_p \Delta T$</td></tr>
</table>

e.g. E matches with: _1_, _4_, _7_, _8_, _10_, ….

A matches with: 2, 5, 6, 8, 10, ….
B matches with: 3, 8, 10,____, ….
C matches with: 7, 8, 9, 10____, ….
D matches with: 5, 6, 7, 8, 10 ….
The cycle ABCDE matches with: 5, 6, 8, 10

2. (6 points)

a) Use your knowledge of thermodynamics to explain why oil and water don't mix at room temperature. (1-2 sentences only please)

Oil molecules group together to free water molecules from forming the surrounding cages. Freeing the water molecules increases the mobility of molecules dramatically, thereby increasing the overall entropy of the solution.

b) In the real world, if you start with a cup of chicken-noodle soup and a cup of milk at the same temperature (and same volume) and put them on your kitchen table, after a few minutes the temperatures of both cups will be different from each other. Why?
One sentence should suffice to answer this question.

The two liquids have different heat capacities, therefore for the same amount of heat lost to the table, they will achieve different temperatures ($q=C\,\Delta T$)

c) Why do manufacturers make automobile engines that run hotter today than they did 80 years ago?

The efficiency of the engine depends on the temperatures of the hot and cold reservoir (see eq). Therefore the hotter the explosion (hot reservoir) the higher the efficiency.

3. (16 points)
a).Calculate the standard Gibbs energy, the standard Enthalpy and the standard Entropy for the reaction at 298.15 K (use data in the data section).

$$\mathrm{CH_4(g) + 2Cl_2(g) \rightarrow CCl_4(g) + 2H_2(g)}$$

$$\Delta_r G^0 = \sum_{\text{prod}} \nu \Delta_f G^0(\text{prod}) - \sum_{\text{react}} \nu \Delta_f G^0(\text{react})$$

ΔG^0=-58.20-(-50.72)= -7.48 kJ/mol

$$\Delta_r S^0 = \sum_{prod} \nu S_m^0(prod) - \sum_{react} \nu S_m^0(react)$$

From data, ΔS^0 = -61.5 J K^{-1} mol^{-1}

$$dG = dH - d(TS)$$

$\Delta H = \Delta G + T\,\Delta S$ = -7.48 + (298.15)(-0.0615) = -25.82 kJ/mol b). If the partial pressures for the reactants and products at 298.15 K are 1500 Pa for methane, 300 Pa for chlorine, 200 Pa for tetrachloromethane, and 1000 Pa for hydrogen. Will the reaction under these conditions tend to generate more products?

$$\Delta G = \Delta G^o + RT\ln\left(\frac{\left(\frac{p_C}{p^o}\right)^c\left(\frac{p_D}{p^o}\right)^d}{\left(\frac{p_A}{p^o}\right)^a\left(\frac{p_B}{p^o}\right)^b}\right)$$

$$\Delta_r G = -7480\frac{J}{mol} + \left(8.314\frac{J}{Kmol}\right)(298K)\ln\left(\frac{\left(\frac{1000}{101325}\right)^2\left(\frac{200}{101325}\right)}{\left(\frac{300}{101325}\right)^2\left(\frac{1500}{101325}\right)}\right)$$

$$\Delta_r G = -6506\frac{J}{mol}$$

Negative, therefore spontaneous as written.

Reaction will generate more products.

Note that if you get to the same conclusion by comparing Q and K, that is ok also.

c). Calculate the numerical value for the equilibrium constant for this reaction.

$$\ln K = -\frac{\Delta_r G^o}{RT}$$

$\ln K = -\frac{-4780}{8.314\ 298.15}$

K = 20.4

4. (4 points) Estimate the standard enthalpy of formation of $(CH_3)_3C\text{-}CClH\text{-}CH_3$ using Benson thermochemical groups.

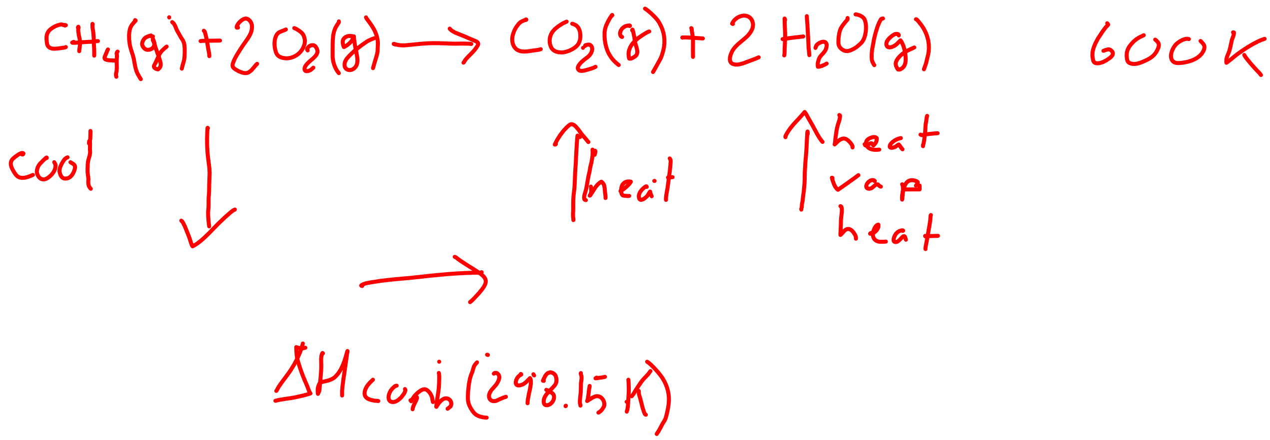
From left to right:

$$\Delta_f H = 3\Delta_f H(C(H)_3C) + \Delta_f H(C(C)_4) + \Delta_f H(C(Cl)(H)C_2) + \Delta_f H(C(H)_3C)$$

$$\Delta_f H = 3(-42.17) + 8.16 + (-60.2) + (-42.17)$$

$$\Delta_f H = -220.7kJ/mol$$

5. (10 points) At 600K, the reaction of methane gas with oxygen gas will produce carbon dioxide and water vapor. What is the $\Delta_r H$ for this reaction at 600K?
Hint: mind the phase transition.



$$\Delta_{rxn}H = nC_{p,m}(Me)\Delta T + nC_{p,m}(O_2)\Delta T$$
$$+ n\Delta_{comb}H(Me) +$$
$$nC_{p,m}(CO_2)\Delta T + nC_{p,m}(H_2O,l)\Delta T + n\Delta_{vap}H(H_2O) + nC_{p,m}(H_2O,g)\Delta T$$

$$\Delta_{rxn}H = 1mol(35.31JK^{-1}mol^{-1})(298K - 600K) + 2mol(29.36JK^{-1}mol^{-1})(298K - 600K)$$
$$+1mol(-891000Jmol^{-1}) +$$
$$1mol(37.11JK^{-1}mol^{-1})(600K - 298K) +$$
$$2mol(89.10JK^{-1}mol^{-1})(373K - 298K) + 2mol(-40660Jmol^{-1}) + 2mol(33.58JK^{-1}mol^{-1})(600K - 373K)$$

$$\Delta_{rxn}H = -770100J = -770.1kJ$$

6. (5 points) Calculate the entropy change for the process below (one mol).
Hint: mind the phase transition.

H_2O, l (300K, 1atm) → H_2O, g (400K, 1atm)

Three steps, heat liquid, evaporate at 373K, heat gas

$\Delta S_T = \Delta S_{l \rightarrow 373} + \Delta S_{l \rightarrow g\ (at373)} + \Delta S_{g \rightarrow 400}$

$$\Delta S_T = nC_{p,m,l}\, ln\left(\frac{373.15}{T_1}\right) + n\frac{\Delta H_{vap}}{373.15} + nC_{p,m,g}\, ln\left(\frac{T_2}{373.15}\right)$$

$\Delta S_T = 130.7$ J/K

7. (5 points) Consider the equilibrium reaction below. If the vapour pressure at 273.15 K is 611 Pa. Calculate the sublimation pressure of ice (the gas pressure) at 232.89 K, assuming that all enthalpy changes are constant over this range of temperatures.

$H_2O, s \rightleftharpoons H_2O, g$

Plug an play into: $\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_{sub}H_m}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

Remember $K = \frac{P_g/_{P^0}}{P_s/_{P^0}}$ and $P_s/_{P^0} = 1$ *for any solid or liquid*

So $\ln\left(\frac{P_{g2}/P^0}{P_{g1}/P^0}\right) = -\frac{\Delta_{sub}H_m}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

And $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

$$\ln\frac{p_2}{611Pa} = -\frac{40670\ J\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1}}\left(\frac{1}{232.89\ K}-\frac{1}{273.15\ K}\right)$$

$p_2 = 17.5$ Pa

8. (6 points) Calculate the change in Helmholtz free energy (ΔA) when one mole of a real gas (van der Waals) is expanded from 1 L to 5 L at a constant temperature of 300K. (a = 1.5 atm L^2 mol^{-2}, b = 0.035 L mol^{-1})
Start from the exact differential ($dA = -pdV - SdT$).

$dA = -pdV - SdT$ dT=0 $p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$

$$\int dA = \int -pdV = \int -nRT\frac{1}{V-nb}dV + \int an^2V^{-2}dV$$

$$\Delta A = \int dA = -nRT\ln\left(\frac{V_2-nb}{V_1-nb}\right) + an^2\left(\frac{1}{V_1}-\frac{1}{V_2}\right)$$

Note: You need the unit conversion of a(atm L^2 mol^{-2}) x101325 Pa/atm x 10^{-3} m^3/L

$\Delta A = -3963J$

Data section:

STP = 0°C and 1 atm SATP = 298.15 K and 1 bar
1 atm = 1.01325 bar = 101325 Pa = 760 torr 1 L = 10^{-3} m^3
R = 8.314 J K^{-1} mol^{-1}

$\Delta_f G^0(CH_4) = -50.72 kJ/mol$ $\Delta_f G^0(CCl_4) = -58.20 kJ/mol$

$\Delta_f G^0(Cl_2) = 0$ $\Delta_f G^0(H_2) = 0$

$C_{p,m}(H_2O, g) = 33.58 JK^{-1}mol^{-1}$ $C_{p,m}(H_2O, l) = 89.10 JK^{-1}mol^{-1}$

$C_{p,m}(He, g) = 20.77 JK^{-1}mol^{-1}$ $C_{p,m}(CO_2, g) = 37.11 JK^{-1}mol^{-1}$

$C_{p,m}(CH_4, g) = 35.31 JK^{-1}mol^{-1}$ $C_{p,m}(O_2, g) = 29.36 JK^{-1}mol^{-1}$

$\Delta_{fusion}H^0(H_2O, T = 273.15K) = 6.01 kJ/mol$

$\Delta_{vaporization}H^0(H_2O, T = 373.15K) = 40.66 kJ/mol$

$\Delta_{combustion}H^0(CH_4, g) = -891 kJ/mol$ $S^0(CO_2, g) = 213.8 Jmol^{-1}K^{-1}$

$S^0(H_2O, l) = 70.0 Jmol^{-1}K^{-1}$ $S^0(O_2, g) = 205.2 Jmol^{-1}K^{-1}$

$S^0(CH_4, g) = 186.3 Jmol^{-1}K^{-1}$ $S^0(CCl_4, g) = 309.6 Jmol^{-1}K^{-1}$

$S^0(H_2, g) = 130.7 Jmol^{-1}K^{-1}$ $S^0(Cl_2, g) = 223.1 Jmol^{-1}K^{-1}$

Gas phase Benson groups and other relevant data
$\Delta_f H_m^o$(C(H)$_3$(C)) = -42.17 kJ/mol
$\Delta_f H_m^o$(C(H)$_2$(C)$_2$) = -20.7 kJ/mol
$\Delta_f H_m^o$(C(H)(C)$_3$) = -6.91 kJ/mol
$\Delta_f H_m^o$(C(C)$_4$) = 8.16 kJ/mol
$\Delta_f H_m^o$(C(Cl)(H)(C)$_2$) = -60.2 kJ/mol

Potentially useful formulas:

If $a = f(x)$ and $b = f(x)$ then $d(ab) = a \cdot db + b \cdot da$

If $a = f(x, y)$ then $da = \left(\frac{\partial a}{\partial x}\right)_y dx + \left(\frac{\partial a}{\partial y}\right)_x dy$

$\boxed{pV = nRT}$ $\quad Z = \frac{pV}{nRT} = \frac{pV_m}{RT}$ $\quad$ ` $p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$

$pV_m = RT\left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + ...\right)$

$dU = dw_{exp} + dw_{other} + dq$ $\quad \Delta U = w + q$ $\quad \Delta U = q_v = C_v \Delta T$

$\Delta U = q = IVt$

$w = -\int_{V_i}^{V_f} p\,dV$ $\quad w = -p_{ext}\Delta V$ $\quad w = -nRT \ln \frac{V_f}{V_i}$

$w = \Delta U = C_V \Delta T$ $\quad w = -nR(T_B - T_A)$ $\quad w = -nRT \ln\left(\frac{p_A}{p_B}\right)$

$H = U + pV$ $\quad dH = dU + d(pV)$ $\quad dH = dU + d(nRT)$

$\Delta H = q_p = C_p \Delta T$ $\quad q = nRT \ln \frac{V_f}{V_i}$

$C_p = \left(\frac{\partial H}{\partial T}\right)_p$ $\quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$ $\quad \frac{C_{p,m}}{(\text{J K}^{-1}\ \text{mol}^{-1})} = a + bT + \frac{c}{T^2}$

$\frac{T_B}{T_A} = \left(\frac{V_A}{V_B}\right)^{\gamma - 1}$ $\quad C_p - C_V = nR$ $\quad \gamma = \frac{C_{p,m}}{C_{V,m}}$

$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T$ $\quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ $\quad \left(\frac{\partial T}{\partial P}\right)_H = \mu$ $\quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$ $\quad dU = \pi_T dV + C_V dT$

$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$ $\quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$ $\quad \left(\frac{\partial \left(\frac{\partial x}{\partial y}\right)_z}{\partial z}\right)_y = \left(\frac{\partial \left(\frac{\partial x}{\partial z}\right)_y}{\partial y}\right)_z$

$\Delta_r H(T_2) = \Delta_r H(T_1) + \sum C_p^{prod} \Delta T - \sum C_p^{react} \Delta T$

$\Delta_r H^0 = \sum_{prod} \nu H_m^0(\text{prod}) - \sum_{react} \nu H_m^0(\text{react})$ $\quad \Delta_r S^0 = \sum_{prod} \nu S_m^0(prod) - \sum_{react} \nu S_m^0(react)$

$\Delta_{fus} H^o = H^o(l) - H^o(s)$

$\oint \delta w_{rev} = -\oint \delta q_{rev}$ $\quad$ $\text{Carnot} - \text{Efficiency} = \frac{\left|\oint w\right|}{q_{AB}} = \frac{\left(T_{high} - T_{low}\right)}{T_{high}}$

$dS = \frac{dq_{rev}}{T}$ $\quad$ $dS \geq \frac{dq}{T}$ $\quad$ $dS_{Tot} = dS_{sys} + dS_{surr}$

$\Delta_{mix}S = \sum_{i=1}^{N} n_i R \ln\left(\frac{V_{final}}{V_{i,initial}}\right)$ $\quad$ $\Delta_{trs}S^o = \frac{\Delta_{trs}H^o}{T_{trs}}$ $\quad$ $\Delta S = \int_{T1}^{T2} \frac{C\,dT}{T} = C\ ln\frac{T_2}{T_1}$

$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$ $\quad$ $\Delta_{mix}S_m = -R\sum_{n=1}^{N} \chi_i \ln \chi_i$ $\quad$ $\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)$

$dA = dU - d(TS)$ $\quad$ $\Delta A = -nRT\ln\left(\frac{V_{final}}{V_{initial}}\right)$

$H = U + pV$

$dH = dU + d(pV)$

$dG = dH - d(TS)$

$\Delta_r G^0 = \sum_{prod} \nu\Delta_f G^0(\text{prod}) - \sum_{react} \nu\Delta_f G^0(\text{react})$ $\quad$ $G_j(p_j) = G_j^{\,o} + n_j RT\ln\left(\frac{p_j}{p^o}\right)$

$\Delta G = \Delta G^o + RT\ln\left(\frac{\left(\frac{p_C}{p^o}\right)^c\left(\frac{p_D}{p^o}\right)^d}{\left(\frac{p_A}{p^o}\right)^a\left(\frac{p_B}{p^o}\right)^b}\right)$ $\quad$ $\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$ $\quad$ $\ln K = -\frac{\Delta_r G^o}{RT}$

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

$dU = dw + dq = TdS - pdV$

$dH = dU + d(pV) = TdS - pdV + pdV + Vdp = TdS + Vdp$

$dA = dU - d(TS) = TdS - pdV - TdS - SdT = -pdV - SdT$

$dG = dH - d(TS) = TdS + Vdp - TdS - SdT = Vdp - SdT$

$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ $\quad$ $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$ $\quad$ $-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p = V\alpha$