Name:
Student Number:

CHM 2131
Midterm Test, October 24th 2014

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.
Feel free to remove these pages.

Maximum score = 63/60 points

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

1. (11 points) 10 g of ethanol vapour (C_2H_5OH) is combusted under standard pressure at 298 K.

a) What is the total enthalpy of combustion for this reaction?

$$C_2H_5OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$$

$$\Delta_r H_m^\circ = \sum_{\text{Products}} v\Delta_f H_m^\circ - \sum_{\text{Reactants}} v\Delta_f H_m^\circ$$

$$= 3\Delta_f H_m^\circ\left(H_2O_{(l)}\right) + 2\Delta_f H_m^\circ\left(CO_{2(l)}\right) - \Delta_f H_m^\circ\left(C_2H_5OH_{(l)}\right) - 3\Delta_f H_m^\circ\left(O_{2(l)}\right)$$

$$= 3\left(-285.83\ \text{kJ mol}^{-1}\right) + 2\left(-393.51\ \text{kJ mol}^{-1}\right) - \left(-235.10\ \text{kJ mol}^{-1}\right)$$

$$= -1409.41\ \text{kJ mol}^{-1}$$

$$\Delta_r H^o = n\Delta_r H_m^\circ$$

$$= \frac{m}{M} \times \Delta_r H_m^\circ$$

$$= \frac{10\ \text{g}}{46.07\ \text{g mol}^{-1}}\left(-1409.41\ \text{kJ mol}^{-1}\right)$$

$$= -310\ \text{kJ}$$

kJ, not per mol

b) What would the total enthalpy be for combustion of liquid ethanol at the same temperature?

$$\Delta_r H_m^\circ(\text{liquid ethanol}) = \Delta_r H_m^\circ(\text{ethanol vapor}) + \Delta_{vap} H_m^\circ(\text{liquid ethanol})$$

$$= -1409.41\ \text{kJ mol}^{-1} + 43.5\ \text{kJ mol}^{-1}$$

$$= -1365.91\ \text{kJ mol}^{-1}$$

$$\Delta_r H^o = n\Delta_r H_m^\circ$$

$$= \frac{m}{M} \times \Delta_r H_m^\circ$$

$$= \frac{10\ \text{g}}{46.07\ \text{g mol}^{-1}}\left(1365.91\ \text{kJ mol}^{-1}\right)$$

kJ, not per mol

$$= -296\ \text{kJ}$$

c) What would be the total enthalpy for the combustion of the vapour at 350 K?

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

$$\Delta_r H(350) = -1409410 J/mol + 89.1 J/Kmol(350K - 298K) + 2(37.11 J/Kmol)(350 - 298)$$
$$- 3(29.36 J/Kmol)(350 - 298) - 64.44 J/Kmol(350 - 298)$$

$$\Delta_r H(350) = -1409410 + 4633.2 + 3547.44 - 4580.16 - 3350.88 = -1409160 J/Kmol$$

$$\Delta_r H(350) = -1409.16 kJ / Kmol$$
$$for 10g \Delta_r H(350) = -305.87 kJ$$

2. (10 points) For the following reaction at 298 K, the partial pressures for the reactants and products are 500 Pa for methane, 600 Pa for chlorine, 200 Pa for tetrachloromethane, and 850 Pa for hydrogen.

$$CH_4(g) + 2Cl_2(g) \leftrightarrow CCl_4(g) + 2H_2(g)$$

a) Will the reaction under these conditions tend to generate more products?

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

$$\Delta_r G^0 = -58.2 \frac{kJ}{mol} + 50.72 = -7.48 \frac{kJ}{mol}$$

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

$$\Delta_r G = -7480 \frac{J}{mol} + \left(8.314 \frac{J}{Kmol}\right)(298K) \ln \left(\frac{\left(\frac{850}{101325}\right)^2 \left(\frac{200}{101325}\right)}{\left(\frac{600}{101325}\right)^2 \left(\frac{500}{101325}\right)} \right)$$

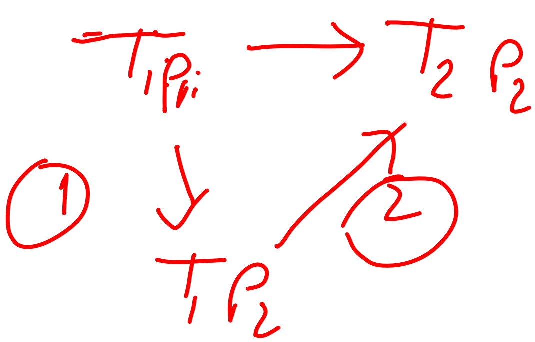
$$\Delta_r G = -8024 \frac{J}{mol}$$

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.

3.a (7 points) Find the change in entropy for 2.50 mol of argon when it is cooled from 400 K to 300 K while at the same time expanding so that its pressure decreases from 4 bar to 1 bar.



$$\Delta S_T = \Delta S_1(\text{constant temperature}) + \Delta S_2(\text{constant pressure})$$

Since entropy is as state function, you can chose any path you like.

$$\Delta S_T = nR\ln\left(\frac{V_{\text{int}}}{V_1}\right) + nC_p\ln\left(\frac{T_2}{T_1}\right)$$

Notice that the volume is changing, so the intermediate volume is $V_{\text{int}} = \frac{nRT_1}{p_2}$ if you follow this cycle (isothermal + isobaric).

Also, $V_1 = \frac{nRT_1}{p_1}$, so

$$\Delta S_T = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_{\text{int}}}{V_1}\right) = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{p_1}{p_2}\right)$$

$$\Delta S_T = 2.5mol\left(20.77JK^{-1}mol^{-1}\right)\ln\left(\frac{300K}{400K}\right) + 2.5mol\left(8.314JK^{-1}mol^{-1}\right)\ln\left(\frac{4bar}{1bar}\right)$$

$$\Delta S_T = -14.9JK^{-1} + 28.8JK^{-1} = 13.9JK^{-1}$$

3.b (5 points) If the change occurs in two steps, isobaric followed by isothermal, calculate the work done.

$$w_T = w_{isobaric}(\text{constant pressure}) + w_{isothermal}(\text{constant temperature})$$

$$w_T = -p_1\left(V_{\text{int}} - V_1\right) - nRT_2\ln\left(\frac{V_2}{V_{\text{int}}}\right)$$

For this path: $V_{\text{int}} = \frac{nRT_2}{p_1}$ and also $V_1 = \frac{nRT_1}{p_1}$ and $V_2 = \frac{nRT_2}{p_2}$

$$w_T = -4x10^5\,Pa\left(0.0154m^3 - 0.0205m^3\right) - 2.5mol\left(8.314JK^{-1}mol^{-1}\right)(300K)\ln\left(\frac{0.0615m^3}{0.0154m^3}\right)$$

$$w_T = 2040J - 8634J = -6594J$$

4. (5 points) Estimate the standard enthalpy of formation of $(CH_3)_2CH\text{-}CH_2\text{-}CClH$ – $(CH_2)_3\text{-}CH_3$ using Benson thermochemical groups.

$\Delta H = 3\ CH_3 + 4\ CH_2 + 1\ CH + 1\ CClH$

$\Delta H = -276.42\ kJ/mol$

5. (6 points) Consider the systems below, for the following processes indicate whether ΔT, ΔU, ΔH, q, and w is greater than, less than or equal to zero. (Write >0, <0, or =0)

a) An ideal gas isothermally and irreversibly expands into a vacuum.

ΔT → __=0___, ΔU → __=0___, ΔH→ _=0____, q→ __=0___, w→ _=0____

b) A balloon filled with an ideal gas undergoes an expansion without a change in pressure.

ΔT → __>0___, ΔU → __>0___, ΔH→ _>0____, q→ __>0___, w→ _<0____

c) An ice cube melting in a cup. (The density of liquid water is greater than that of solid ice.)

ΔT → _=0____, ΔU → ___>0__, ΔH→ __>0___, q→ __>0___, w→ __<0___

6. (6 points) Calculate the maximum work available (ΔA) through the combustion of methane, on a per mol basis at 298 K and 1 bar pressure. Write the balanced equation.

Equation: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$dA = dU - d(TS)$$
$$\Delta A = \Delta U - T\Delta S$$
$$\Delta A = \Delta_c H - \Delta nRT - T\{S^0(CO_2) + 2 * S^0(H_2O(l)) - 2 * S^0(O_2) - S^0(CH_4)\}$$
$\Delta A = -813.6kJ$ per mol of methane

7. (10 points) Mark the following statements as true or false.

NOTE: YOU WILL LOOSE MARKS FOR INCORRECT ANSWERS.

	T/F
a) The internal energy of an ideal gas is independent of temperature.	F
b) The total entropy of the universe is always increasing.	T
c) A gas that expands spontaneously and irreversibly against an external pressure is performing work.	T
d) The change in entropy of a mixing process is always negative.	F
e) The ΔG^0 for a process in equilibrium is equal to zero.	F
f) The efficiency of an engine is independent of temperature.	F
g) The Helmhotz free energy change for a process provides the maximum amount of work that the process can do.	T
h) Entropy is a state function.	T
i) The molar entropy of a gas contained in 1.0 L at 298 K is higher than the molar entropy of a gas contained in 1.0 L at 450 K.	F
j) ΔH for any phase transition is always positive.	F

8. (3 points) Consider a case where you leave two identical cups with identical volumes of fluid at the same temperature on the counter. One cup contains water and the other hot chocolate. Your observation is that when you check 10 minutes later, one cup is hotter than the other. Use your knowledge of thermodynamics to explain why in one or two sentences.

The two liquid have different heat capacities. i.e. they require different amounts of energy to cool each degree.

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}

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

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

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

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

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

$C_{p,m}(CH_3CH_2OH, g) = 64.44 JK^{-1}mol^{-1}$

$C_{p,m}(CH_3CH_2OH, l) = 111.46 JK^{-1}mol^{-1}$

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

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

$\Delta_{combustion}H^0(CH_4, g) = -891 kJ/mol$

$\Delta_{vaporization}H^0(C_2H_5OH, T = 298.15K) = 43.50 kJ/mol$

$\Delta_f H_m^o(H_2O(l)) = -285.83$ kJ mol^{-1} $\Delta_f H_m^o(H_2O(g)) = -241.82$ kJ mol^{-1}

$\Delta_f H_m^o(CO_2(g)) = -393.51$ kJ mol^{-1} $\Delta_f H_m^o(C_2H_5OH(g)) = -235.10$ kJ mol^{-1}

$M(C_2H_5OH) = 46.07$ g mol^{-1}

$S^0(CO_2, g) = 213.8 Jmol^{-1}K^{-1}$

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

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

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

$\Delta_f H_m^o(C(H)_3(C))$ = -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 $da = \left(\frac{\partial a}{\partial x}\right)_y dx + \left(\frac{\partial a}{\partial y}\right)_x dy$

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

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

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

$\Delta U = q = IVt$

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

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

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

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

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

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

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

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

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

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

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

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

$$\oint \delta w_{rev} = -\oint \delta q_{rev}$$

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

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

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

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

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

$$H = U + pV$$

$$dH = dU + d(pV)$$

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

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

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

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

$$dU = dw + dq = TdS - pdV$$

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

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

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

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

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