Name:
Student Number:

CHM 2132
Midterm Test, October 24^{th} 2008

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.
You can remove these pages and keep them.

Maximum score = 58/55 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?

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

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

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

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

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

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

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

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

$$= -310\text{ kJ mol}^{-1}$$

kJ, not per mol

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

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

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

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

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

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

kJ, not per mol

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

$$= -296\text{ kJ mol}^{-1}$$

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

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

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

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

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

2. (5 points) Estimate the standard enthalpy of formation of $(CH_3)_3C\text{-}CClH\text{-}CH_3$ using Benson thermochemical groups.

From left to right:

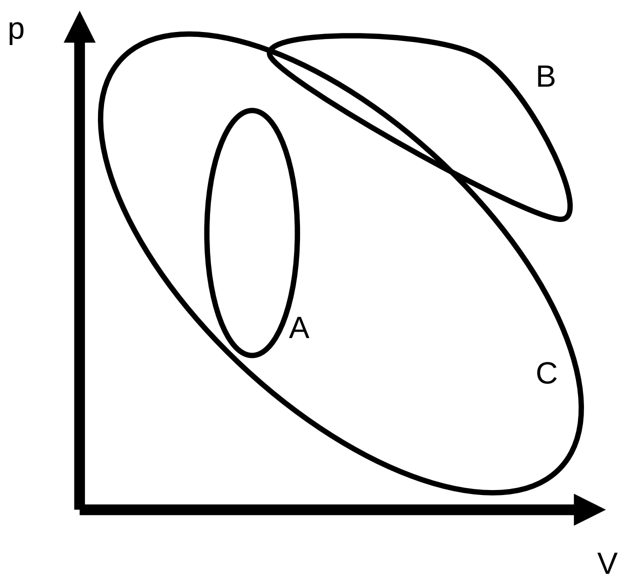
$$\Delta_f H = 3\Delta_f H(C(H)_3 C) + \Delta_f H(C(C)_4) + \Delta_f H(C(Cl)(H)C_2) + \Delta_f H(C(H)_3 C)$$
$$\Delta_f H = 3(-42.17) + 8.16 + (-60.2) + (-42.17)$$

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

3. (12 points)

a) Each one of the loops below represents a heat engine. Explain in ONE sentence which engine is capable of producing more work and why.

The magnitude of work is given by the area inside the loop, therefore loop C is the one capable of producing more work.



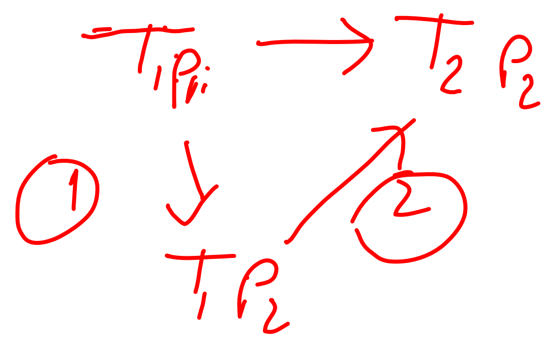
b) Mark the following statements as true or false.

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 for a process in equilibrium is equal to zero.	T
f) The ΔG^0 for a process in equilibrium is equal to zero.	F
g) The Helmhotz free energy change for a process provides the maximum amount of work that the process can do.	T
h) The Gibbs free energy change for a process provides an indication of spontaneity for constant volume processes.	F
i) ΔH for any phase transition is always positive.	F

4. (7 points) Find the change in entropy for 2.50 mol of argon when it is cooled from 500 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 $V_{\text{int}} = \dfrac{nRT_1}{p_2}$ if you follow this cycle (isothermal + isobaric).

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

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

$$\Delta S_T = 2.5mol\left(20.77JK^{-1}mol^{-1}\right)\ln\left(\frac{300K}{500K}\right) + 2.5mol\left(8.314JK^{-1}mol^{-1}\right)\ln\left(\frac{4bar}{1bar}\right)$$

$$\Delta S_T = -26.5JK^{-1} + 28.8JK^{-1} = 2.3JK^{-1}$$

5 (6 points) 1.2 mol of an ideal gas is trapped in a piston at equilibrium with its surroundings at 0.5 atm and 298.15 K. The gas then undergoes an isothermal reversible expansion from a volume of 2.50 L to 10.0 L. The molar constant-volume heat capacity of this gas is 27.5 J K^{-1} mol^{-1}.

a) What is the final pressure of the gas? State your final answer in a sentence.

$$p_2 = \frac{1.2mol * 8.314JK^{-1}mol^{-1} * 298.15K}{10L * 10^{-3}m^3L^{-1}} = 297458Pa$$

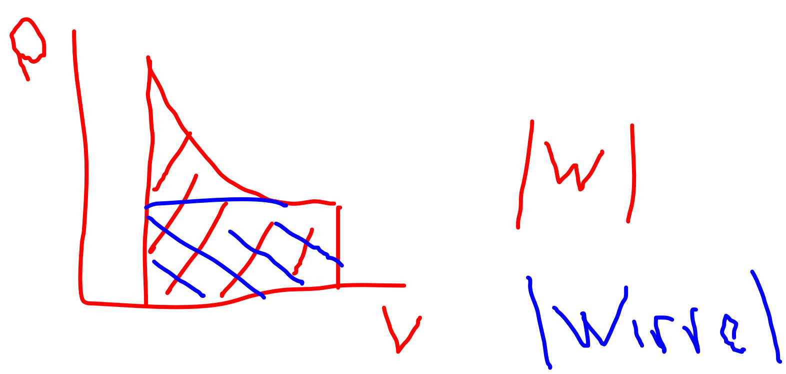
(You could also do this as p1V1=p2V2)

b) What is the total work and the total heat of this process?

$$w = -nRT\ln\frac{V_f}{V_i} = -1.2mol * 8.314J/Kmol * 298.15 * \ln\left(\frac{10}{2.5}\right) = -4123J = -q$$

c) Is it possible for this gas to do more work without giving the system any more energy? Briefly explain your answer using *p*-*V* diagrams.

For expansion work, the maximum work that the gas can do is reversible. Therefore the gas in this example cannot do more work.



6. (10 points) For the following reaction at 298 K, the partial pressures for the reactants are 500 Pa for methane, 600 Pa for chlorine, 200 Pa for tetrachloromethane, and 850 Pa for hydrogen. Will the reaction under these conditions tend to generate more products?

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

solution

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

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

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

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

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

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.

7. (4 points) In the first step of glucose metabolism the following two reactions are coupled to give glucose-6-phosphate (G6P) and ADP under standard conditions at 25°C:

1) Glucose(aq) + phosphate(aq) $\rightarrow$ G6P(aq) + H_2O(l) ΔG^o = 14.3 kJ
2) ATP(aq) + H_2O(l) $\rightarrow$ ADP(aq) + phosphate(aq) ΔG^o = -31.0 kJ

a) What is the Gibbs free energy for the following reaction under standard conditions?

Glucose(aq) + ATP(aq) $\rightarrow$ G6P(aq) + ADP(aq)

$$\Delta_r G^0 = 14.3 - 31.0 = -16.7 kJ$$

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

$$\ln K = -\frac{\Delta_r G^o}{RT}$$ (1) $$\ln K = \frac{16700}{8.314 * 298} = 6.74$$ K=846

8. BONUS (3 points) Calculate the isothermal compressibility coefficient at 5000 Pa, of a gas whose compressibility is 0.5.

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad Z = \frac{pV}{nRT} = 0.5$$

$$V = nRTZp^{-1}$$

substitute and derive

$$\kappa_T = -\frac{1}{V}\left(-nRTZp^{-2}\right) = \frac{1}{p} = \frac{1}{5000\,Pa}$$

Note: if you substituted the ideal gas law, it is wrong, even if in the end Z cancels out.

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}

$\Delta_f G^0(CH_4) = -50.72 kJ/mol$ $\Delta_f G^0(CCl_4) = -58.20 kJ/mol$
$\Delta_f G^0(Cl_2) = 0$ $\Delta_f G^0(H_2) = 0$
$C_{p,m}(H_2O, g) = 33.58 JK^{-1}mol^{-1}$ $C_{p,m}(H_2O, l) = 89.10 JK^{-1}mol^{-1}$
$C_{p,m}(Ar, g) = 20.77 JK^{-1}mol^{-1}$ $C_{p,m}(CO_2, g) = 37.11 JK^{-1}mol^{-1}$
$C_{p,m}(CH_4, g) = 35.31 JK^{-1}mol^{-1}$ $C_{p,m}(O_2, g) = 29.36 JK^{-1}mol^{-1}$
$C_{p,m}(CH_3CH_2OH, g) = 64.44 JK^{-1}mol^{-1}$
$C_{p,m}(CH_3CH_2OH, l) = 111.46 JK^{-1}mol^{-1}$
$\Delta_{fusion} H^0(H_2O, T = 273.15 K) = 6.01 kJ/mol$
$\Delta_{vaporization} H^0(H_2O, T = 373.15 K) = 40.66 kJ/mol$
$\Delta_{combustion} H^0(CH_4, g) = -891 kJ/mol$
$\Delta_{vaporization} H^0(C_2H_5OH, T = 298.15 K) = 43.50 kJ/mol$
$\Delta_f H_m^o(H_2O(l)) = -285.83$ 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}
$S^0(CO_2, g) = 213.8 Jmol^{-1}K^{-1}$ $S^0(CH_4, g) = 186.3 Jmol^{-1}K^{-1}$
$S^0(H_2O, l) = 70.0 Jmol^{-1}K^{-1}$ $S^0(O_2, g) = 205.2 Jmol^{-1}K^{-1}$

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

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

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

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

$\Delta U = q = IVt$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$dS = \frac{dq_{rev}}{T}$$

$$dS \geq \frac{dq}{T}$$

$$dS_{Tot} = dS_{sys} + dS_{surr}$$

$$\Delta_{mix}S = \sum_{i=1}^{N} n_i R \ln\left(\frac{V_{final}}{V_{i,initial}}\right)$$

$$\Delta_{trs}S^o = \frac{\Delta_{trs}H^o}{T_{trs}}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

$$\Delta_{mix}S_m = -R\sum_{n=1}^{N} \chi_i \ln \chi_i$$

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)$$

$$dA = dU - d(TS)$$

$$\Delta A = -nRT\ln\left(\frac{V_{final}}{V_{initial}}\right)$$

$$H = U + pV$$

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

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

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

$$G_j(p_j) = G_j^{\,o} + n_j RT\ln\left(\frac{p_j}{p^o}\right)$$

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

$$\left(\frac{\partial\left(\Delta G/T\right)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

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

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

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

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

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

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

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

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

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

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