Name: Student Number:

CHM 2131
Midterm Test, October 20 2017

Read carefully:

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in your obtaining a **0** (zero) for the exam.

By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

Signature: ______________________________

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.

Q1 ______________/8

Q2 ______________/6

Q3 ______________/16

Q4 ______________/4

Q5 ______________/10

Q6 ______________/4

Q7 ______________/5

Q8 ______________/4

Maximum score = 57 / 55

1. Consider the following processes:

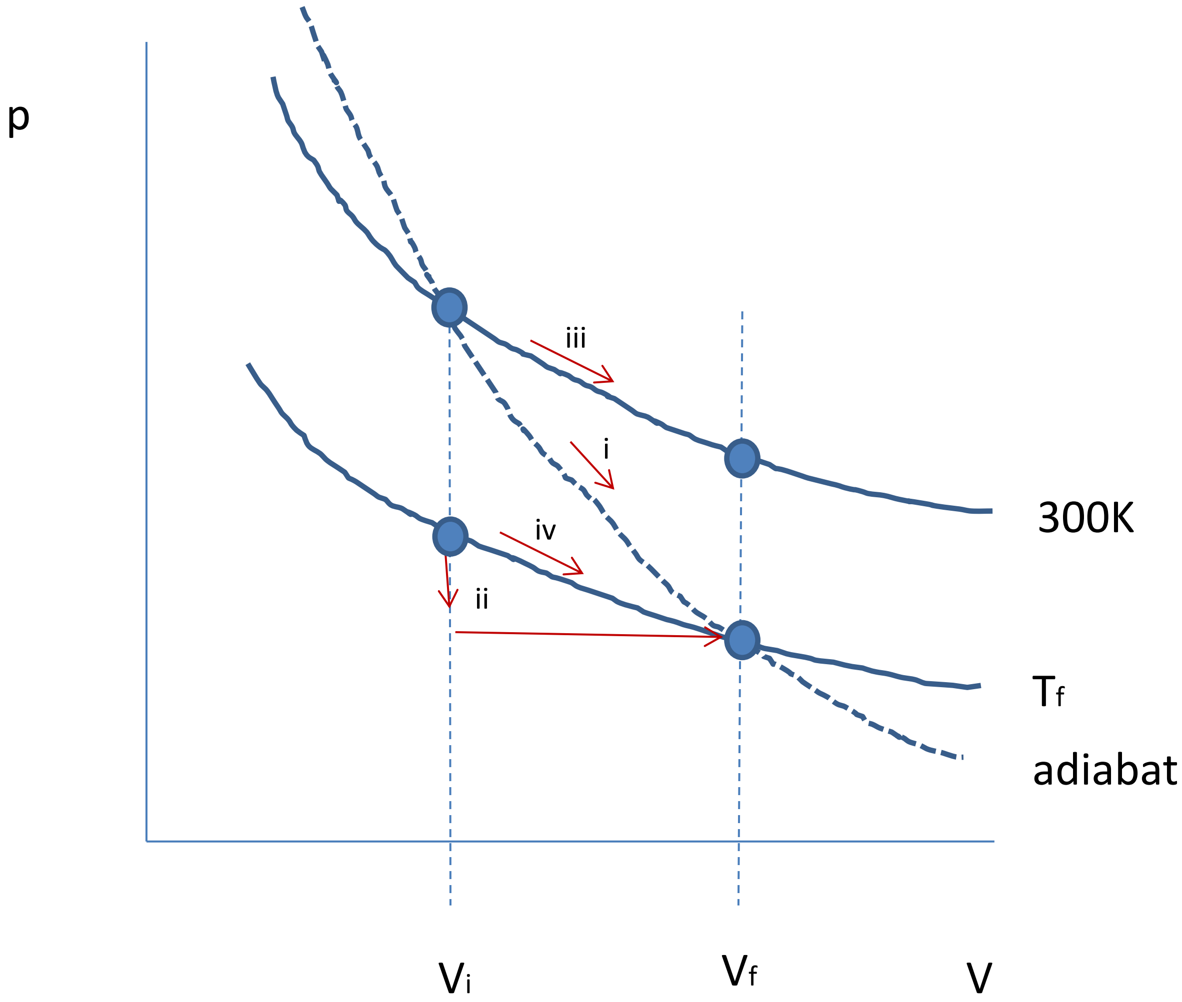
i)reversible expansion of a monoatomic ideal gas from T=300K and V_i to T_f and V_f.

ii)irreversible isothermal expansion of a monoatomic ideal gas at $T=T_f$ (final temperature achieved in i) from V_i to V_f.

iii)reversible isothermal expansion of a monoatomic ideal gas at T=300K from V_i to V_f.

iv) reversible isothermal expansion of a monoatomic ideal gas at $T=T_f$ (final temperature achieved in i) from V_i to V_f.

a) (4 points) Draw the four processes in one P-V diagram with appropriate labels



b) (4 points) Arrange the processes in order of increasing work done by the system.

Explain using the diagram in a.

Magnitude of work is given by the area under the curve.

ii < iv < i < iii

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).

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

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

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.

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

$\ln K = -\frac{-7480}{8.314\ 298.15}$

K = 20.4

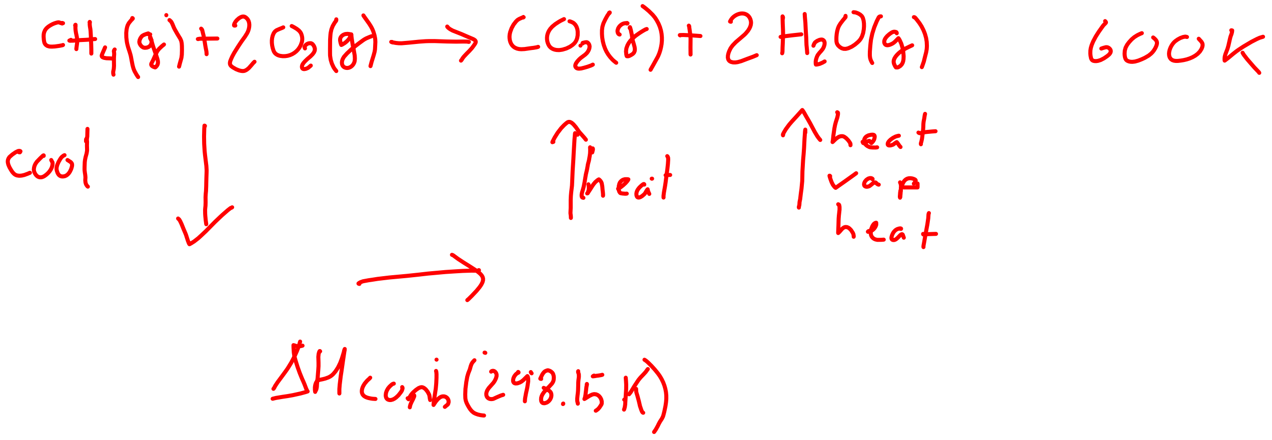
4. (4 points) Estimate the standard enthalpy of formation of $(CH_3)_3C\text{-}CClH\text{-}CH_3$ using Benson thermochemical groups.

From left to right:

$$\Delta_f H = 3\Delta_f H(C(H)_3C) + \Delta_f H(C(C)_4) + \Delta_f H(C(Cl)(H)C_2) + \Delta_f H(C(H)_3C)$$
$$\Delta_f H = 3(-42.17) + 8.16 + (-60.2) + (-42.17)$$

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

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.



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

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

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

6. (4 points) The change in the Gibbs energy of a certain constant pressure process was found to fit the expression:

$$\Delta G(in\, J) = -85.40 + 36.5(\,K^{-1})\,T$$

Calculate the value of ΔS for the process.

dG = dH – d(TS) = TdS + Vdp – TdS – SdT = Vdp – SdT $\left(\frac{\partial G}{\partial T}\right)_p = -S$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

$$\Delta S = -\left(\frac{\partial(-85.40 + 36.5(\,K^{-1})\,T)}{\partial T}\right)_p = -36.5\, J/K$$

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

$$\ln\frac{p_2}{611Pa} = -\frac{46670\, J\, mol^{-1}}{8.314\, J\, K^{-1}\, mol^{-1}}\left(\frac{1}{232.89\, K} - \frac{1}{273.15\, K}\right)$$

p_2 = 17.5 Pa

8. (4 points) Consider an ideal gas at 1dm^3 and 2.0 bar. If the gas is compressed isothermally at constant external pressure so that V_f = 0.5dm^3, a) what is the value of the external pressure? And b) Calculate the work involved.

$P_f V_f = p_i V_i$

$$p_f = \frac{2bar\ x\ 1\ L}{0.5\ L} = 4\ bar$$

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

$$w = -4bar\left(\frac{10^5 Pa}{bar}\right)(0.5 - 1L)\left(\frac{10^{-3} m^3}{L}\right) = 200\ Pa\ m^3\ = 200\ J$$

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

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

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

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

$$\Delta U = q = IVt$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\Delta S = \int_{T1}^{T2} \frac{C\,dT}{T} = C \ln\frac{T_2}{T_1}$$

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

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

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

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

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

$$H = U + pV$$

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

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

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

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

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

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

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

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

$$\mathrm{dU = dw + dq = TdS - pdV}$$

$$\mathrm{dH = dU + d(pV) = TdS - pdV + pdV + Vdp = TdS + Vdp}$$

$$\mathrm{dA = dU - d(TS) = TdS - pdV - TdS - SdT = -pdV - SdT}$$

$$\mathrm{dG = dH - d(TS) = TdS + Vdp - TdS - SdT = Vdp - SdT}$$

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

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{S}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{p}}$$

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

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