

CHEM 323
Fall 2008
In-Class Portion of Exam 1

Name: _____

Instructions

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it.

Show all work for full credit! For the word problems write your final answer in complete sentences. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

You may use the back of any page as additional workspace. Please indicate that you have done so.

There are **9** pages, **0** blank.

If you have any questions regarding the exam, please ask me. I will attempt to answer them, if I can, without giving away the answer.

Problem	Possible Points	Points Received
1	12	
2	20	
3	15	
4	13	
5	7	
6	10	
Free	23	23
Total	100	
	Bonus	
	Grand Total	

1a. (6 Points) An alternative way to relate enthalpy and entropy is given by the Planck function, Y , defined by the equation $Y = S - \frac{H}{T}$. Prove that, at constant pressure, the criterion for spontaneous change is $dY \geq 0$. Hint: start with the Clausius inequality and use the definitions of H , U and w as needed.

The easy way.

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

The Clausius inequality.

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

At constant p , $dq = dH$ by definition.

$$dS - \frac{dH}{T} + \frac{H}{T^2} dT \geq 0$$

Rearranging and adding $\frac{H}{T^2} dT$, which does not change the inequality.

$$Y \geq 0$$

The left hand side of the equation is simply the definition of the Planck function in differential form.

The hard way.

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

The Clausius inequality.

$$dS \geq \frac{dU - dw}{T}$$

Solving $dU = dq + dw$ for dq and substituting.

$$dS \geq \frac{dH - pdV - Vdp - dw}{T}$$

Rearranging the definition of H in differential form ($dH = dU + pdV + Vdp$) and substituting.

$$dS \geq \frac{dH - pdV - Vdp + pdV}{T}$$

Substituting the definition of work in differential form ($dw = -pdV$).

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

Simplifying and applying condition of constant pressure ($dp = 0$).

$$dS - \frac{dH}{T} + \frac{H}{T^2} dT \geq 0$$

Rearranging and adding $\frac{H}{T^2} dT$, which does not change the inequality.

$$Y \geq 0$$

The left hand side of the equation is simply the definition of the Planck function in differential form.

b. (6 Points) Since the Planck function is a state function, we may write the differential

$dY = \left(\frac{\partial Y}{\partial T}\right)_p dT + \left(\frac{\partial Y}{\partial p}\right)_T dp$. Using the definition of Y from part a, $Y = S - \frac{H}{T}$, and the definitions

of H , U and other thermodynamic parameters, demonstrate that for a reversible process

$$\left(\frac{\partial Y}{\partial T}\right)_p = \frac{H}{T^2} \text{ and } \left(\frac{\partial Y}{\partial p}\right)_T = -\frac{V}{T}.$$

$$dY = dS - \frac{dH}{T} + \frac{H}{T^2} dT$$

Differential of $Y = S - \frac{H}{T}$.

$$dY = dS - \frac{dU + pdV + Vdp}{T} + \frac{H}{T^2} dT$$

Substituting the definition of H in differential form $dH = dU + pdV + Vdp$.

$$dY = dS - \frac{dq + dw + pdV + Vdp}{T} + \frac{H}{T^2} dT$$

Substituting the First Law ($dU = dq + dw$).

$$dY = dS - \frac{dq + Vdp}{T} + \frac{H}{T^2} dT$$

Substituting the definition of work in differential form ($dw = -pdV$) and simplifying.

$$dY = \frac{dq}{T} - \frac{dq + Vdp}{T} + \frac{H}{T^2} dT$$

Substituting the definition of S for reversible change ($dS = \frac{dq}{T}$).

$$dY = -\frac{V}{T} dp + \frac{H}{T^2} dT$$

Simplifying.

By comparison of the equation $dY = \left(\frac{\partial Y}{\partial T}\right)_p dT + \left(\frac{\partial Y}{\partial p}\right)_T dp$ and $dY = -\frac{V}{T} dp + \frac{H}{T^2} dT$, it

is clear that $\left(\frac{\partial Y}{\partial T}\right)_p = \frac{H}{T^2}$ and $\left(\frac{\partial Y}{\partial p}\right)_T = -\frac{V}{T}$.

2a. (7 Points) A sample consisting of 0.500 moles of helium gas is expanded isothermally and reversibly from a volume of 2.00 L to 10.0 L at 27.0 °C. Determine w , q , and ΔS for this process. You may assume that He behaves as an ideal gas under these conditions with $C_{V,m} = \frac{3}{2}R$.

For an isothermal reversible expansion of an ideal gas $\Delta U = 0$, therefore $q = -w$.

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -(0.500 \text{ mole})\left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)(300.15 \text{ K})\ln\left(\frac{10.0 \text{ L}}{2.00 \text{ L}}\right)$$

$$w = -(1.247 \text{ kJ})\ln(5.00) = -2.01 \text{ kJ}$$

The entropy change may be calculated as follows.

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = (0.500 \text{ mole})\left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)\ln(5.00) = +6.69 \frac{\text{J}}{\text{K}}$$

For this process $q = +2.01 \text{ kJ}$, $w = -2.01 \text{ kJ}$ and $\Delta S = +6.69 \text{ J/K}$.

b. (10 Points) If this expansion occurred reversibly and adiabatically, what would be w , q , and ΔS for the process?

For a reversible adiabatic process $\Delta S = 0$ and $\Delta U = w$, since $q = 0$. For an ideal gas the change in the internal energy depends only on T , therefore we can integrate the

expression $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ to give $\Delta U = C_V \Delta T$ (assuming C_V is independent of T). We

need to find T_f , which we may calculate from $V_i T_i^c = V_f T_f^c$, where $c = \frac{C_{V,m}}{R}$. Solving for

T_f and substituting the value of $c (= 3/2)$ gives $T_f^{3/2} = \frac{V_i}{V_f} T_i^{3/2}$, which may be written as

$$T_f = \left(\frac{V_i}{V_f}\right)^{2/3} T_i \text{ . Substituting gives } T_f = \left(\frac{2.00 \text{ L}}{10.0 \text{ L}}\right)^{2/3} (300.15 \text{ K}) = 102.64 \text{ K . Therefore,}$$

$\Delta T = -197.5 \text{ K}$ and

$$w = \Delta U = nC_{V,m} \Delta T = \left(\frac{3}{2}\right)(0.500 \text{ mole})\left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)(-197.5 \text{ K}) = -1.23 \text{ kJ}$$

So, the reversible adiabatic expansion of an ideal gas initially at 27.0 °C from 2.00 L to 10.0 L has $q = 0$, $\Delta S = 0$ and $w = -1.23 \text{ kJ}$.

c. (3 Points) Explain the differences in the values you found in part *a* and *b* of this question.

The first thing to note is that the system does not end up in the same state at the end of each process. Even though the final volumes are the same, the temperatures are very different and so the states (as defined by the state variables n , p , V and T) are different. So while we expect the path functions q and w to be different (because the final volume was achieved in different ways), ΔS is also different because we are not arriving at the same final state.

3a. (3 Points) Using the thermodynamic data given below (at 25.00 °C) the temperature at which the reaction $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ becomes spontaneous at standard pressure is 370.11 K.

Species	$\Delta_f H^\circ$ (kJ/mole)	S° (J/K·mole)	$\Delta_f G^\circ$ (kJ/mole)
$\text{H}_2\text{O}(\text{l})$	-285.830	69.91	-237.129
$\text{H}_2\text{O}(\text{g})$	-241.818	188.825	-228.572

Explain why this isn't 373.15 K.

Ignoring the small difference between standard (1 bar) and normal pressure (1 atm), both ΔH and ΔS for this reaction change as a function of temperature. Therefore, the values at the boiling point are not the same as those under standard conditions and we would expect a small difference between the predicted and actual boiling points.

b. (7 Points) Derive an equation that relates the boiling point temperature at standard pressure, T_b , to ΔH° (298.15 K) and ΔS° (298.15) showing that corrects the problems you identified in part *a*.

At the boiling point there is no direction of spontaneous change because both the liquid and gas are equally thermodynamically stable. Therefore, $\Delta G = 0$ and at constant

pressure $T_b = \frac{\Delta_{\text{vap}} H}{\Delta_{\text{vap}} S}$ (by rearranging $\Delta G = \Delta H - T\Delta S$), where T_b is the boiling

temperature and $\Delta_{\text{vap}} H$ and $\Delta_{\text{vap}} S$ are the enthalpy and entropy changes associated with the process, respectively. By substituting in the equations that describe how $\Delta_{\text{vap}} H$ and $\Delta_{\text{vap}} S$ change from 298.15 to T_b , we get the following.

$$T_b = \frac{\Delta H(298.15) + \int_{298.15}^{T_b} \Delta_r C_p dT}{\Delta S(298.15) + \int_{298.15}^{T_b} \frac{\Delta_r C_p}{T} dT}$$

c. (2 Points) What approximation would you make to simplify this equation?

We could assume that the heat capacities of both liquid and gaseous water are independent of temperature, which would allow us to pull them outside the integrals.

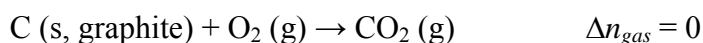
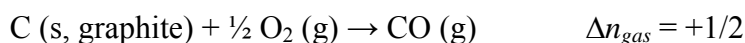
d. (3 Points) This equation still has a problem. What is it? Suggest a way to overcome it.

The boiling point appears on both sides of the equation. In essence, we would have to know the boiling point to calculate the integral so that we could calculate the boiling point. The way around it is to use the method of successive approximation (or other iterative method) where we would start with a guess of what T_b is and use this to evaluate the integrals and calculate a new T_b . This new T_b would be then used to repeat the process until a value of T_b was obtained that was constant at the desired level of precision.

4a. (8 Points) An internal energy of formation, $\Delta_f U^0$ (defined in the same way as enthalpies of formation, $\Delta_f H^0$) may be calculated from the corresponding $\Delta_f H^0$. From the data given below calculate $\Delta_f U^0$ for CO_2 and CO at 298.15 K. Assume all gases are ideal.

Species	$\Delta_f H^0$ (kJ/mole)	S^0 (J/K·mole)	$\Delta_f G^0$ (kJ/mole)
CO (g)	-110.53	197.67	-137.17
CO ₂ (g)	-393.51	213.74	-394.36
O ₂ (g)	0	205.138	0

If we know ΔH , then we can find ΔU since $\Delta H = \Delta U + \Delta(pV)$. If we assume that the gases involved are ideal and that the volumes of any solids do not contribute to the overall volume, we can rewrite this as $\Delta H = \Delta U + \Delta n_{gas} RT$ or $\Delta U = \Delta H - \Delta n_{gas} RT$. To do this we need to know the formation reactions for CO and CO_2 .



Since $\Delta n_{gas} = 0$ for the formation of CO_2 (g), $\Delta_f U^0 = \Delta_f H^0 = -393.51$ kJ/mole.

The calculation for $\Delta_f U^0$ (CO, g) is as follows.

$$\Delta U = \Delta H - \Delta n_{gas} RT = -110.53 \text{ kJ} \cdot \text{mole}^{-1} - \left(+ \frac{1}{2} \right) (8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}) (298.15 \text{ K})$$

$$\Delta U = -110.53 \text{ kJ} \cdot \text{mole}^{-1} - (1.2394_7 \text{ kJ} \cdot \text{mole}^{-1}) = -111.76_9 \text{ kJ} \cdot \text{mole}^{-1}$$

So $\Delta_f U^0$ (CO, g) = -111.77 kJ/mole and $\Delta_f U^0$ (CO₂, g) = -393.51 kJ/mole.

b. (5 Points) Determine ΔU^0 for the reaction $2 \text{CO} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{CO}_2 (\text{g})$.

For this reaction as written

$$\Delta U^0 = (2 \text{ mole}) \Delta_f U^0 (\text{CO}_2, \text{g}) - (2 \text{ mole}) \Delta_f U^0 (\text{CO}, \text{g}) - (1 \text{ mole}) \Delta_f U^0 (\text{O}_2, \text{g})$$

But $\Delta_f U^0 (\text{O}_2, \text{g}) = 0$ by definition. So the equation becomes

$$\Delta U^0 = (2 \text{ mole})(-393.51 \text{ kJ/mole}) - (2 \text{ mole})(-111.77 \text{ kJ/mole}) = -563.48 \text{ kJ}$$

For this reaction $\Delta U^0 = -563.48 \text{ kJ}$.

c. What is ΔA^0 for this reaction at 298.15 K? (Post-Exam question)

The definition of A is $A = U - TS$. In differential form this is $dA = dU - TdS - SdT$. If we evaluate this at a constant temperature (298.15 K, in this case) and assuming that U and S are independent of T we may integrate to obtain $\Delta A = \Delta U - T\Delta S$ (which is analogous to the equation $\Delta G = \Delta H - T\Delta S$).

Determine ΔS for the reaction.

$$\Delta S = (2 \text{ mole}) \left(213.74 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right) - (2 \text{ mole}) \left(197.67 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right) - (1 \text{ mole}) \left(205.138 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right)$$

$$\Delta S = -173.00 \frac{\text{J}}{\text{K}}$$

Substitute ΔS and ΔU into the equation $\Delta A = \Delta U - T\Delta S$ and solve for ΔA .

$$\Delta A = \Delta U - T\Delta S = -563.48 \text{ kJ} - (298.15 \text{ K}) \left(-173.00 \frac{\text{J}}{\text{K}} \right)$$

$$\Delta A = -563.48 \text{ kJ} + 51.579, \text{ kJ} = -511.90 \text{ kJ}$$

For this reaction $\Delta A = -511.90 \text{ kJ}$.

5. (7 Points) The designers of four heat engines, each claiming to produce 1000 watts of useful output power, have come to you seeking money to commercialize their designs. The designers make the following claims: Engine A needs 900 watts of heat input, Engine B requires 1500 watts of heat input, Engine C requires 2500 watts and Engine D requires 3000 watts. Each heat engine operates between a two temperature reservoirs, one at 200.0 °C and one at 0.0 °C. Which engine do you invest your money in and why? Show calculations for full credit. FYI 1 watt = 1 J·s⁻¹.

Since power is work per unit time, we can just use the equation $\varepsilon = \frac{|w|}{q_h}$ and substitute in power for $|w|$ and q_h since the time units will cancel. Or we could simply recognize that efficiency is power out divided by power in. Note that all calculations done to three significant figures although this is totally arbitrary because the number of significant figures in the given information is not clearly indicated.

Engine	Efficiency
A	$\varepsilon = \frac{1000 \text{ watts}}{900 \text{ watts}} = 1.11$
B	$\varepsilon = \frac{1000 \text{ watts}}{1500 \text{ watts}} = 0.667$
C	$\varepsilon = \frac{1000 \text{ watts}}{2500 \text{ watts}} = 0.400$
D	$\varepsilon = \frac{1000 \text{ watts}}{3000 \text{ watts}} = 0.333$

Engine A is clearly impossible because it does more work than energy it takes in.

Engine B looks to be the best, but perhaps it is too good. The best heat engine that we can make is a Carnot engine which requires perfect reversibility. The efficiency of the Carnot engine depends only on the temperature of the hot and cold reservoirs. Its efficiency is given by the equation $\varepsilon_{rev} = 1 - \frac{T_c}{T_h}$. Thus the maximum efficiency of a heat

engine operating between the given reservoirs is $\varepsilon_{rev} = 1 - \frac{273.15 \text{ K}}{473.15 \text{ K}} = 1 - 0.5773 = 0.423$.

Engine B is, therefore, also impossible as it exceeds the maximum efficiency for a heat engine operating between the given reservoirs.

One must then choose Engine C as it has the maximum efficiency without violating the Second Law of Thermodynamics (as Engines A and B did).

6. (10 Points) For copper at 293.0 K the isothermal compressibility, κ_T , is $0.735 \times 10^{-6} \text{ atm}^{-1}$. Compare the pressure required to give a 0.050% decrease in copper's volume with that required to bring about the same change in an equal volume of He at 1.00 atm of pressure and 293.0 K. Treat He as an ideal gas.

Rearrange the expression for κ_T ($\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$) to give $\kappa_T dp = -\frac{1}{V} dV$. Integrate this expression on both sides, assuming κ_T is independent of T , and solve for Δp .

$$\kappa_T \int dp = -\int \frac{1}{V} dV$$

$$\kappa_T \Delta p = -\ln \left(\frac{V_f}{V_i} \right)$$

$$\Delta p = \frac{-\ln \left(\frac{V_f}{V_i} \right)}{\kappa_T}$$

The definition of ΔV is $\Delta V = V_f - V_i$, which we can rearrange and solve for V_f . Substituting this result into the expression for Δp gives the following expression.

$$\Delta p = \frac{-\ln \left(\frac{V_i + \Delta V}{V_i} \right)}{\kappa_T} = \frac{-\ln \left(1 + \frac{\Delta V}{V_i} \right)}{\kappa_T}$$

The value of $\Delta V/V_i$ is -5.0×10^{-4} (from the given % decrease in volume). Substituting this and the value of κ_T into the above expression gives Δp .

$$\Delta p = \frac{-\ln \left(1 + \frac{\Delta V}{V_i} \right)}{\kappa_T} = \frac{-\ln(1 - 5.0 \times 10^{-4})}{0.735 \times 10^{-6} \text{ atm}^{-1}} = \frac{5.0 \times 10^{-4}}{0.735 \times 10^{-6} \text{ atm}^{-1}} = 6.8 \times 10^2 \text{ atm}$$

Note that $\ln(1 \pm x) = \pm x$ for $x \ll 1$, which is the case here.

For an ideal gas

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial}{\partial p} \left(\frac{nRT}{p} \right) \right)_T = \frac{1}{V} \left(\frac{nRT}{p^2} \right) = \frac{1}{p^2} \left(\frac{nRT}{V} \right) = \frac{1}{p}$$

So, at 1.00 atm $\kappa_T = 1.00 \text{ atm}^{-1}$. Substituting this value of κ_T into the Δp expression above, gives $\Delta p = 5.0 \times 10^{-4} \text{ atm}$.

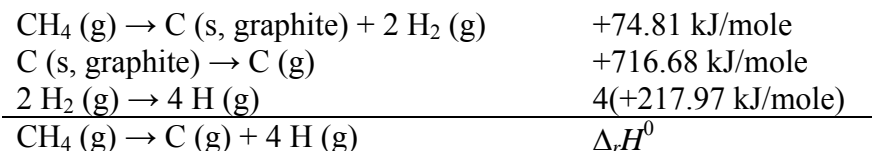
Post-Exam Question. From the $\Delta_f H^0$ for C (g), H (g) and CH₄ (g), calculate the C–H bond dissociation enthalpy.

We have the following reactions.



We want the reaction CH₄ (g) → C (g) + 4 H (g), because one-fourth of its $\Delta_f H^0$ is the enthalpy associated with breaking one C–H bond (i. e., the bond dissociation enthalpy).

We can then use Hess's Law to write



and

$$\Delta_r H^0 = 74.81 + 716.68 + 4(+217.97) \text{ kJ/mole} = +1663.37 \text{ kJ/mole}$$

So, the bond dissociation enthalpy is 415.843 kJ/mole. *Note that we don't need to indicate the '+' sign because bond dissociation enthalpies are always positive.*