Chemistry 452 July 23, 2014

Enter answers in a Blue Book Midterm
Examination

Useful Constants:

- 1 Newton=1 N= 1 kg m s^{-2}
- 1 Joule=1J=1 N m=1 kg m^2/s^2
- 1 Pascal=1Pa=1N m^{-2}
- 1atm=101325 Pa
- 1 bar=10^5 Pa
- 1L=0.001m^3
- Universal Gas Constant R=8.31 J K^{-1} mol^{-1}=0.0821L atm $K^{-1}mol^{-1}$
- Avagadro's Number N_A=6.024x10^{23} mol^{-1}

All answers must be in SI units (i.e. units of meters, seconds, kilograms, Joules, Pascals, Kelvin degrees etc.)

Helpful math relationships:

1) $\frac{dax^n}{dx} = anx^{n-1};$ a is a constant, n is a positive or negative number

2) $\int x^n dx = \frac{x^{n+1}}{n+1} dx + c$ where c is a constant and $n \neq -1$

3) $\int \frac{dx}{x} = \ln x + c$ where c is a constant

4) $\ln(xy) = \ln x + \ln y; \ln\left(\frac{x}{y}\right) = \ln x - \ln y; x \ln y = \ln y^x$

Part 1 (18 points) Answer THREE out of the following SIX questions. Limit definitions to less than 200 words. Use equations where helpful or required, but detailed calculations are not necessary.

Question 1.1. In Chemistry 452 and Chemistry 456 the First Law of Thermodynamics is given as $\Delta U = q + w$. But in thermal physics and engineering thermodynamics courses the First Law has the form $\Delta U = q - w$. Explain the reasons for these two versions of the First Law.

Solution: The different versions of the first law arise from differences in the sign conventions for work In the convention used in chemistry work done by the system is negative w<0 and work done on the system is positive w>0. In this convention $\Delta U = q + w$. In engineering/physics work done by the system is positive w>0 and work done on the system is negative w<0. The conventions for heat transfer are identical. For heat transfer out of the system q<0, and transfer into the system q>0. This results in a sign change for work in the first law expression $\Delta U = q - w$

Question 1.2 The internal energy U is an exact differential and has the form for a closed system: $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$. Explain the physical meanings of $\left(\frac{\partial U}{\partial T}\right)_V$ and $\left(\frac{\partial U}{\partial V}\right)_T$. What are the values of these terms for an ideal monatomic gas? Explain.

Solution: $\left(\frac{\partial U}{\partial T}\right)_V$ is the heat capacity, the degree to which internal energy changes per a unit change in temperature. A high heat capacity indicates a high capacity to absorb heat. For an ideal monatomic gas $\left(\frac{\partial U}{\partial T}\right)_V$ =3R/2. $\left(\frac{\partial U}{\partial V}\right)_T$ is the internal pressure, the change of internal energy per unit change in volume. The internal pressure reflects the magnitude of intermolecular interactions. For an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T$ =0.

Question 1.3 **Which of the following types of work are quantified by the Gibbs energy at constant pressure and temperature? A) Pressure-volume work; B) electrical work (i.e. moving charge through a electrical potential gradient); C) osmotic work (i.e. moving solute mass through a concentration gradient) ; D) elastic work (i.e. stretching an elastic fiber). Explain your answer.**

Solution: The definition of the Gibbs function:

dG=dH-d(TS)=TdS-PdV+dwother+PdV+VdP-TdS-SdT=dwother-SdT+VdP. If dT=dP=0 then dG=dwother, Therefore PV work is not reflected by the Gibbs function while electrical, osmotic and elastic work are included in the Gibbs function.

Question 1.4 Explain how the entropy limits the efficiency of a heat engine. You may use the Carnot engine as an example in your explanation. You may use equations to assist in your explanation, but detailed calculations are not necessary.

Solution: A Carnot Cycle consists of 1) an isothermal expansion at T_H ; 2) an adiabatic expansion; 3) an isothermal compression at T_C; 4) an adiabatic compression. Therefore the entropy change over one cycle $q_H/T_H+q_C/T_C=0$. For the entropy to sum to zero over a cycle $q_C=q_HT_C/T_H$ must be nonzero.

Question 1.5: For an adiabatic reversible expansion the entropy change is zero. But for an adiabatic irreversible change the entropy is not zero. Explain.

Solution: For any adiabatic change q=0. If the adiabatic change is reversible then $q_{rev}=0$ and so $\Delta S=q_{rev}/T=0$. For an irreversible change $q_{rev}>q_{irrev}=0$ and in this case $\Delta S=q_{rev}/T>0$.

Question 1.6 As the temperature of an atomic crystal is increased, what value does the heat capacity approach? Explain.

Solution: The heat capacity approaches 3R. There are two degrees of freedom per dimension so the heat capacity per dimension is 2xR/2=R. Foe vibration in three dimensions the heat capacity is 3R.

Part 2: (20 points) Answer TWO of the FOUR questions. Answers longer than 200 words are acceptable but numerical calculations are not required. Physical reasoning based on thermodynamic principles is recommended. Equations may be used to illustrate your points.

Problem 2.1 Explain the following observation. Burns caused by contact between skin and steam at 373K are far more severe than burns caused by contact between the skin and liquid water at 373K. Use the appropriate state function in your explanation. Assume heat is transferred at constant pressure.

Solution: A burn from hot water results from the transfer of heat from the water to the skin. A burn from steam results first from heat transfer from the steam to the skin, then the steam condenses on the skin transferring more heat. Further heat transfer results from the liquid water after it condenses on the skin.

Problem 2.2 Suppose a liquid is converted reversibly to its vapor at its normal boiling point. State whether the following thermodynamic quantities are positive, negative, or zero: q, w, ΔV, ΔT, ΔH, ΔS, ΔG.

Solution:

$q>0$, $w<0$, $\Delta V>0$, $\Delta T=0$, $\Delta H>0$, $\Delta S>0$, $\Delta G=0$.

Problem 2.3) Differential scanning calorimetry (DSC) measures directly the enthalpy of denaturation of a protein. Call the enthalpy of denaturation measured by DSC ΔH_{DSC}. A second way to obtain the enthalpy of denaturation supposes at any temperature the equilibrium constant is $K=\frac{f_D}{f_N}=\frac{f_D}{1-f_D}$ where f_D is the fraction of denatured protein and f_N is the fraction of structured protein. The van't Hoff equilibrium equation states that if the equilibrium constant is measured at two different temperatures, i.e. by measuring f_D at two different temperatures, the enthalpy can be calculated from:

$$\ln\left(\frac{K_2}{K_1}\right)=-\frac{\Delta H_{vH}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

where ΔH_{vH} is called the van't Hoff enthalpy of denaturation. The enthalpy of denaturation of the same protein is measured repeatedly by these two methods and it is found consistently that $\Delta H_{vH} \ll \Delta H_{DSC}$. Assuming absence of systematic experimental errors, explain why this might be so.

Solution: DSC is a direct measure of the heat absorbed by all protein forms in solution within a given temperature range. The van't Hoff equation given above assumes only two protein forms are in solution and only two forms of the protein are assumed to absorb heat. Therefore the van't Hoff equation may under-estimate the amount of heat absorbed.

Problem 2.4) The solar flux is the rate at which energy from the sun passes through a unit area on the surface of the earth per unit time. Suppose the solar flux warms the water at the surface of a lake to T=300K. Because water at the bottom of the lake is at T=280K, a temperature gradient is produced. Heat transferred from the warmer surface water to the cooler water at the lake bottom can used to run a heat engine which produces energy at a rate of 5×10^6 Watts (i.e. 5 MW). Assume the solar flux at the lake surface is about 500 Watts per squared meter (i.e. $500 Wm^{-2}$) and the lake has an area of $10000 m^2$. Can the engine function as described? Does the engine obey the first law of thermodynamics? Does it obey the second law of thermodynamics? Explain.

Solution: The total average energy flux into the lake is $(500\ W/m^2)\ (10000 m^2)=5\times10^6\ m^2$. Therefore the engine only outputs 20% of the input energy so it obeys the First Law. On the opther hand the efficiency of the engine should be: (300-280)/300=0.067 or 6.7%. So the heat engine violates the Second Law.

Part 3: (30 points) Answer TWO of the FOUR questions.

Problem 3.1: Determine the Gibbs energy change for converting graphite to diamond at P=15,000 atm and T=298K. The following table provides some useful thermodynamic data for graphite and diamond at T=298K and P=1.00 atm. Assume molar volumes are constant over pressure ranges specified. Based on your answer, can diamonds be produced in this way?

	$\Delta G_f^\circ\left(kJmol^{-1}\right)$	$V_m\left(cm^3mol^{-1}\right)$
$C\left(s, graphite\right)$	0	5.33
$C\left(s, diamond\right)$	2.900	3.42

Solution: A diagram is helpful in solving this problem but is not required.

$$
\begin{array}{cccccc}
 & C\left(gr,s\right) & \xrightarrow[P=15000atm,T=298K]{\Delta G} & C\left(dia,s\right) & \\
\Delta P & \uparrow & & \downarrow & -\Delta P \\
 & C\left(gr,s\right) & \xrightarrow[P=1atm,T=298K]{\Delta G_f^\circ} & C\left(dia,s\right) &
\end{array}
$$

Then

$$\Delta G_f^\circ = V\left(gr\right)\Delta P + \Delta G - V\left(dia\right)\Delta P$$

$$\Delta G = \Delta G_f^\circ + \left(V\left(dia\right) - V\left(gr\right)\right)\Delta P$$

$$= 2900\,Jmol^{-1} + \left(3.42\times10^{-6}m^3 - 5.33\times10^{-6}m^3\right)\left(15000atm\right)\left(101325Pa\cdot atm^{-1}\right)$$

$$= 2900\,Jmol^{-1} - 2903\,Jmol^{-1} = -3\,Jmol^{-1}$$

$\Delta G<0$ so this approach works.

Problem 3.2. Between T=273K and T=373K mercury Hg(l) has a heat capacity, in units of $JK^{-1}mol^{-1}$, that is given by: $C_P^{\circ}\left(Hg,\ell\right)=30.093-4.944\times10^{-3}\frac{T}{K}$. Calculate ΔH and ΔS if the temperature of one mole of mercury is raised from T=273K to T=373K.

Solution:

$$\Delta H=\int_{273}^{373}C_P^{\circ}\left(T\right)dT=\int_{273}^{373}\left(30.093-4.944\times10^{-3}\frac{T}{K}\right)dT$$

$$=30.093JK^{-1}mol^{-1}\left(373K-273K\right)-\left(4944\times10^{-3}\right)\left(\frac{373^2-273^2}{2}\right)$$

$$=3009.3J-159.7J=2849.6J$$

$$\Delta S=\int_{273}^{373}\frac{C_P^{\circ}\left(T\right)}{T}dT=\int_{273}^{373}\left(\frac{30.093}{T}-4.944\times10^{-3}\right)dT$$

$$=\left(30.093JK^{-1}mol^{-1}\right)\ln\left(\frac{373}{273}\right)-\left(4.944\times10^{-3}JK^{-1}mol^{-1}\right)\left(373K-273K\right)$$

$$=9.392JK^{-1}-0.4944JK^{-1}=8.899JK^{-1}$$

Problem 3.3 For water at T=300K and P=1 atm, the coefficient of thermal expansion $\beta=3.04\times10^{-4}K^{-1}$ and the isothermal compressibility $\kappa=4.46\times10^{-10}m^2N^{-1}$. Calculate $\left(\frac{\partial U}{\partial V}\right)_T$ for water at T=300K and P=1 atm. Will this value of $\left(\frac{\partial U}{\partial V}\right)_T$ be greater than or less than $\left(\frac{\partial U}{\partial V}\right)_T$ for water at T=383K and P=1atm? Explain.

Solution:

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial P}{\partial T}\right)_V-P=T\frac{\beta}{\kappa}-P=\left(300K\right)\frac{3.04\times10^{-4}K^{-1}}{4.46\times10^{-10}m^2N^{-1}}-101325Nm^{-2}$$

$$=2.045\times10^8Nm^{-2}-1.01\times10^5Nm^{-2}\approx2.045\times10^8Nm^{-2}$$

Water boils at T=373K so at T=383K the water is in vapor form. Intermolecular interactions are smaller in the vapor versus the liquid so $\left(\frac{\partial U}{\partial V}\right)_T$ would be smaller at T=383K than at T=300K

Problem 3.4 Suppose 1 mole of an ideal monatomic gas at an initial temperature of T_1=298K and pressure P_1=1.01x10^6 Pa, expands adiabatically and reversibly until the pressure has dropped to P_2=101325Pa. Calculate the final volume, final temperature, ΔU, and ΔH**.**

Solution:

$$P_1V_1 = nRT_1 \Rightarrow V_1 = \frac{nRT_1}{P_1} = \frac{\left(8.31JK^{-1}\right)\left(298K\right)}{1.01\times10^6\,Pa} = 2.45\times10^{-3}\,m^3$$

$$P_1V_1^\gamma = P_2V_2^\gamma \Rightarrow V_2 = V_1\left(\frac{P_1}{P_2}\right)^{1/\gamma} = \left(2.45\times10^{-3}\,m^3\right)\left(\frac{1.01\times10^6}{1.01325\times10^5}\right)^{3/5} = 9.73\times10^{-3}\,m^3$$

$$T_2 = \frac{P_2V_2}{nR} = \frac{\left(101325Pa\right)\left(9.80\times10^{-3}\,m^3\right)}{8.31JK^{-1}} = 119K$$

$$\Delta U = nC_V\Delta T = \frac{3R}{2}\left(119K - 298K\right) = \left(1.5\right)\left(8.31JK^{-1}\right)\left(-179K\right) = -2231J$$

$$\Delta H = nC_P\Delta T = \frac{5R}{2}\left(119K - 298K\right) = \left(2.5\right)\left(8.31JK^{-1}\right)\left(-179K\right) = -3719J$$

Part 4 (32 points) Perform ONE out of the TWO multi-step calculations

Problem 4.1. In certain bacteria, the amino acid glycine H_2NCH_2COOH is synthesized by a reaction between ammonia NH_3, methane CH_4, and oxygen:

$$NH_3\left(g\right) + 2CH_4\left(g\right) + \tfrac{5}{2}O_2\left(g\right) \rightarrow H_2NCH_2COOH\left(s\right) + 3H_2O\left(\ell\right)$$

Thermodynamic data for this reaction are given in the table below for T=298K and P=1.00 atm.

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	$\Delta H_f^\circ\left(kJmol^{-1}\right)$	$S^\circ\left(JK^{-1}mol^{-1}\right)$	$C_P^\circ\left(JK^{-1}mol^{-1}\right)$
NH_3 (g)	-46.19	192.51	35.66
CH_4 (g)	-74.85	186.19	35.73

O_2 (g)	0	205.03	29.36
H_2NCH_2COOH (s)	-537.23	103.51	99.20
H_2O (l)	-285.84	69.94	75.30

a) Using the data in the table, calculate the enthalpy change ΔH°_{reac} and ΔS°_{reac} for the reaction at T=298K and P=1.00 atm.

Solution:

$$\Delta H^\circ_{reac} = 3\Delta H^\circ_f\left(H_2O,\ell\right) + \Delta H^\circ_f\left(glycine,s\right) - \Delta H^\circ_f\left(NH_3,g\right) - 2\Delta H^\circ_f\left(CH_4,g\right) - \tfrac{5}{2}\Delta H^\circ_f\left(O_2,g\right)$$
$$= (3)(-285.84kJ) - 537.23kJ + 46.19kJ + (2)(74.85kJ) - \left(\tfrac{5}{2}\right)(0) = -1199kJ$$

$$\Delta S^\circ_{reac} = 3S^\circ\left(H_2O,\ell\right) + S^\circ\left(glycine,s\right) - S^\circ\left(NH_3,g\right) - 2S^\circ\left(CH_4,g\right) - \tfrac{5}{2}S^\circ\left(O_2,g\right)$$
$$= (3)\left(69.94JK^{-1}\right) + 103.51JK^{-1} - 192.51JK^{-1} - (2)\left(186.19JK^{-1}\right) - \left(\tfrac{5}{2}\right)\left(205.03JK^{-1}\right)$$
$$= -764JK^{-1}$$

b) Suppose this type of bacterium exists near ocean floor steam vents where the temperature is T=360K. Calculate the enthalpy change and entropy change for this reaction at T=360K. Assume all heat capacities are constant between T=298K and T=360K.

Solution:

$$\Delta C^\circ_P = 3C^\circ_P\left(H_2O,\ell\right) + C^\circ_P\left(glycine,s\right) - C^\circ_P\left(NH_3,g\right) - 2C^\circ_P\left(CH_4,g\right) - \tfrac{5}{2}C^\circ_P\left(O_2,g\right)$$
$$= (3)\left(75.30JK^{-1}\right) + 99.20JK^{-1} - 35.66JK^{-1} - (2)\left(35.73JK^{-1}\right) - \left(\tfrac{5}{2}\right)\left(29.36JK^{-1}\right)$$
$$= 144.6JK^{-1}$$

$$\therefore \Delta H_{reac}(360K) = \Delta H_{reac}(298K) + \Delta C^\circ_P \Delta T = -1199kJ + \left(144.6JK^{-1}\right)(360K - 298K) = -1190kJ$$

$$\Delta S_{reac}(360K) = \Delta S_{reac}(298K) + \Delta C^\circ_P \ln\left(\frac{360}{298}\right) = -764JK^{-1} + \left(144.6JK^{-1}\right)(0.189) = -737JK^{-1}$$

c) Calculate the entropy change of the surrounding and the entropy change for the universe for this reaction at T=360K

Solution:

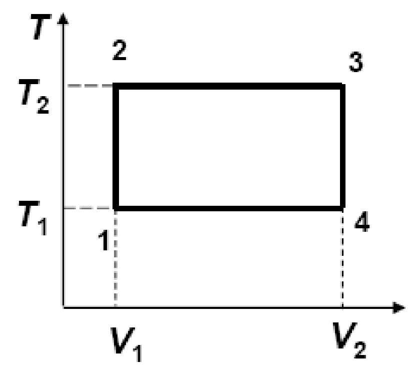
$$\Delta S_{surr} = \frac{-\Delta H(360)}{360K} = \frac{1190000J}{360K} = 3306JK^{-1}$$

$$\Delta S_{universe} = \Delta S_{reac} + \Delta S_{surr} = 3306 JK^{-1} - 737 JK^{-1} = 2569 JK^{-1}$$

d) Based on your answer in part d, will the biosynthesis of glycine in these bacteria proceed spontaneously in the direction written above at T=360K? Explain.

ΔS>0 for universe so reaction will proceed as written

Problem 4.2 : The figure at the right is a four step cycle plotted as a T-V diagram for a Stirling Heat Engine. The Stirling Engine runs reversibly in a clockwise direction (i.e. from point 1 to 2, then to 3, etc.) and operates between a high temperature T_2=400K, and a low temperature T_1=300, and between a maximum volume V_2=0.050m^3 and a minimum volume V_1=0.010m^3. Assume an ideal monatomic gas is the working fluid.



a) For each of the four steps of the Stirling Engine cycle calculate the heat q and the work w.

Solution:

$$w_{12} = 0 \Rightarrow q_{12} = \Delta U_{12} = nC_V \Delta T = \frac{3R}{2}(400K - 300K) = (1.5)(8.31JK^{-1})(100K) = 1247J;$$

$$\Delta U_{23} = 0 \Rightarrow q_{23} = -w_{23} = nRT_2 \ln\left(\frac{V_2}{V_1}\right) = (8.31JK^{-1})(400K)\ln\left(\frac{0.05}{0.01}\right) = 5350J$$

$$w_{34} = 0 \Rightarrow q_{34} = \Delta U_{34} = nC_V \Delta T = \frac{3R}{2}(300K - 400K) = (1.5)(8.31JK^{-1})(-100K) = -1247J$$

$$\Delta U_{41} = 0 \Rightarrow q_{41} = -w_{41} = nRT_1 \ln\left(\frac{V_1}{V_2}\right) = (8.31JK^{-1})(300K)\ln\left(\frac{0.01}{0.05}\right) = -4012J$$

b) Using your results from part a, calculate the total heat absorbed by the Stirling engine in one cycle, the total heat released by the Stirling engine in one cycle, and the net work performed by the engine in one cycle.

Solution:

$$q_{in} = q_{12} + q_{23} = 1247J + 5350J = 6597J$$
$$q_{out} = q_{34} + q_{41} = -1247J - 4012J = -5259J$$
$$w_{net} = w_{12} + w_{23} + w_{34} + w_{41} = 0 - 5350J + 0 + 4012J = -1338J$$

c) Using your results from part b, calculate the efficiency of the Stirling heat engine. Compare this number to the efficiency of a Carnot Engine operating between T_H=400K and T_L=300K.

$$\varepsilon_{Stirling} = \frac{-w_{net}}{q_{in}} = \frac{-(-1338J)}{6597J} = 0.20$$
$$\varepsilon_{Carnot} = \frac{T_H - T_L}{T_H} = \frac{400K - 300K}{400K} = 0.25$$

d) Suppose we run the Stirling engine backwards so that it functions as a refrigerator. Calculate the effectiveness of this refrigerator in removing heat from the low temperature reservoir. Compare this to the effectiveness of a Carnot refrigerator run between the same two temperatures.

$$\varepsilon_{eff,Stirling} = \frac{5259J}{1338J} = 3.93$$
$$\varepsilon_{eff,Carnot} = \frac{T_C}{T_H - T_L} = \frac{300K}{100K} = 3.00$$