Chemistry 452/456
Midterm Examination

Professor G. Drobny

- Universal gas constant: \( R = 8.31 \text{J/mole-K} = 0.0821 \text{L-atm/mole-K} \)
- 1 Joule = 1\( J = 1 \text{Nt-m} = 1\text{kg-m}^2/\text{s}^2 \)
- 101 J = 1 L-atm.
- 1 Pa = 1\( \text{J/m}^3 = 1\text{N/m}^2 \).
- 1 atm = 1.01\( \times 10^5 \) Pa = 1.01 bar
- 1 L = 10\( ^3 \) m\(^3 \).
- 1 Watt = 1 W = 1 Js\(^{-1} \)

2007 Midterm Average = 0.70

- **Give all answers in MKS units:** energy in Joules, pressure in Pascals, volume in \( m^3 \), etc. Only work the number of problems required. Chose wisely.

Part 1: (18 points total) Define 3 out of the following 6 terms as they are used in the fields of thermodynamics and/or mechanics. Keep your definitions brief and to the point. Use of equations, when appropriate, is encouraged, but you need not perform calculations.

1.1) Compare and contrast the reversible and irreversible adiabatic expansions of an ideal gas. In particular, explain how the entropy changes in each case differ and explain the difference.

**Answer:** An adiabatic process occurs in the absence of heat transfer: \( q = 0 \). For a reversible adiabatic process \( q_{rev} = 0 \): \( \Delta S = \frac{q_{rev}}{T} = 0 \). For an irreversible adiabatic process \( q_{irrev} > 0 \): \( \Delta S = \frac{q_{irrev}}{T} > 0 \)

1.2) Define the following properties in terms of partial derivatives of state functions or state variables: the heat capacity at constant pressure, the isothermal compressibility, the thermal expansivity, and the chemical potential. Note in each case under what conditions the partial derivative is calculated.

**Answer:**
- Heat capacity at constant pressure \( C_p = \frac{\partial H}{\partial T} \)
- Thermal Expansivity: \( \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \)
- Isothermal Compressibility: \( \kappa = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \)
- Chemical Potential: \( \mu_i = \frac{\partial G}{\partial n_i} \bigg|_{T,P,n_{(e)}} = \left( \frac{\partial A}{\partial n_i} \right)_{T,Y,n_{(e)}} = \left( \frac{\partial U}{\partial n_i} \right)_{S,Y,n_{(e)}} = \left( \frac{\partial H}{\partial n_i} \right)_{S,P,n_{(e)}} \)
• Note: For a multi-component system, any of the four relationships above for the chemical potential will be sufficient.

1.3) Describe the two types of perpetual motion machines: i.e. perpetual motion machines of the first and second kind. Give an example of each and explain why each cannot exist according to the laws of thermodynamics.

Answer: A perpetual Motion Machine of the first kind violates the first Law of Thermodynamics. It does not conserve energy, e.g. produces work out of nothing. A perpetual motion machine of the second kind violates some aspect of the second law of thermodynamics. For example, a heat engine might conserve energy, but it might transform heat into work with an efficiency that exceeds the second law limit \( \varepsilon = \frac{T_h - T_i}{T_h} \).

1.4) State and explain the third law of thermodynamics. State a practical consequence of this law.

Answer: In any thermodynamic process involving only pure phases at equilibrium the entropy change \( \Delta S \) approaches zero at the absolute zero of temperature, i.e. \( T=0K \). Because of this limiting behavior the absolute entropy (at constant pressure can be measured, i.e. \( S(T) = \int_0^T \frac{C_p(T)}{T} dT \).

1.5) Explain the difference between the Helmholtz and Gibbs energies. In particular relate these two quantities to reversible work.

Answer: The Helmholtz Energy is \( dA = -SdT - PdV + dW_{\text{other}} = -SdT + dW_{\text{rev}} \). The Helmholtz energy therefore measures the isothermal reversible work. For the Gibbs energy: \( dG = -SdT + VdP + dW_{\text{other}} \) so the Gibbs energy measures the reversible non-expansion work at constant \( T \) and \( P \).

1.6) Explain the Second Law of Thermodynamics as it applies to the efficiency of heat engines.

Answer: Assuming the Universe can be treated as an isolated system, as a result of any real process the entropy of the universe must increase. Also, any process whose sole outcome is the complete conversion of heat to work is impossible. The efficiency of any heat engine is therefore limited by \( \varepsilon = \frac{T_h - T_i}{T_h} \) where the temperatures are related by \( T_h > T_i \).

Part 2 (20 points) Answer two out of the four questions below. Answers should be no longer than 200 words. In some cases a brief calculation might be useful and would save a lot of words.

2.1) Before the days of electricity, flatirons for ironing clothes were literally made out of solid iron. They were heated on wood-burning stoves, and had to be quite heavy, despite the fact that anyone could show that it was the heat not the weight of the flatiron that took wrinkles out of clothes. Explain why flatirons had to be so heavy.
Answer: The heat transferred at constant pressure is $MC\Delta T$ where $M$ is the mass, $C$ is the heat capacity and $\Delta T$ is the temperature difference between the cloth and the iron. To maximize heat you have to either maximize $\Delta T$ or $M$. Making $T$ too high is not an option because you would burn the cloth so the mass had to be made large.

2.2) Air is about 80% nitrogen and 20% oxygen. Suppose a sample of air is placed in a chamber which is separated from a second, evacuated chamber by a wall. This entire system is mechanically and thermally isolated from the surroundings. A small pinhole is opened in the wall between the two chambers and the gases effuse through the pinhole into the second chamber. Because nitrogen effuses faster than oxygen, the second chamber fills with nitrogen faster than oxygen, and the two gases thus “unmix” irreversibly, even though the system is isolated from the surroundings. Does the entropy of the isolated system decrease, thus violating the second law? Explain.

Answer: Associated with “unmixing” that results from effusion, the gases expand into a larger volume thus accomplishing a large net entropy increase.

2.3) The equipartition principle predicts that the heat capacity $C_p$ of an ideal monatomic gas is $5R/2$ and the heat capacity of an ideal diatomic gas is $9R/2$. The experimental heat capacity of helium gas is $C_p=20. \text{JK}^{-1} \text{mol}^{-1}$ and the heat capacity of $N_2$ gas is $29.12 \text{J K}^{-1} \text{mol}^{-1}$. Explain any discrepancies between the experimental heat capacities and the predictions of the equipartition theorem.

Answer: Assuming the gases behave ideally, the heat capacities at constant pressure follow the rule: $C_p = C_v + R$. This means that for a ideal monatomic

$$C_p = C_v + R = \frac{3R}{2} + \frac{5R}{2} = 20.78 \text{JK}^{-1} \text{mol}^{-1},$$

reflecting the three degrees of translational freedom possessed by a monatomic. For a diatomic molecule according to the equipartition principle $C_p = C_v + R = \frac{7R}{2} + \frac{9R}{2} = 37.40 \text{JK}^{-1} \text{mol}^{-1}$, reflecting three translational, two rotational, and two vibrational degrees of freedom. While the experimental value for $C_p$ for He agrees with the predicted value, the experimental $C_p$ value for $N_2$ is much closer to $\frac{7R}{2} = 29.09 \text{JK}^{-1} \text{mol}^{-1}$. The two degrees of vibrational freedom are removed because the vibrational energy levels are not thermally populated to any great extent at ambient temperatures. This is a quantum mechanical effect that is not accounted for in the equipartition theorem.

2.4) Water is a polar liquid at ambient temperature with a molecular weight of 0.018 kg mol$^{-1}$. Liquid water has a heat capacity of 75.9 J K$^{-1}$ mol$^{-1}$ and water ice has a heat capacity of about 35.3 JK$^{-1}$ mol$^{-1}$. Argon is a noble gas at ambient temperature and has an atomic weight of 0.018 kg mol$^{-1}$. Liquid argon has a heat capacity of 41.8 JK-1mol-1, and solid argon has a heat capacity of about 30.0 J K$^{-1}$mol$^{-1}$. Why is the difference between
the heat capacities of solid and liquid water so much greater that the difference between
the heat capacities of solid and liquid argon?

Answer: The large difference in the heat capacities of liquid and solid water are believed
by most to arise from the fact that water is a polar molecule and as a consequence is a
highly structured liquid. In the liquid state water molecules are strongly hydrogen
bonded, and when heat is absorbed by liquid water, this energy can break hydrogen
bonds. Another line of thought has it that in liquid water the addition of heat can also
distort hydrogen bonds, changing their length and altering the mutual orientation of water
molecules. None of these effects can occur in argon, which forms a non-polar liquid.
Therefore, while the heat capacity of liquid argon is higher than that of solid argon, the
heat capacity difference is not so great as occurs between liquid and solid water.

Part 3: (30 points) Perform two out of the four calculations given below.

3.1) Suppose five moles of an ideal monatomic gas at an initial volume of 12.2L and
temperature of 298K expand adiabatically and reversibly until the volume has reached
48.8L. Calculate the temperature change $\Delta T$, $\Delta U$, and the work done.

Solution: For a reversible adiabatic change $PV^\gamma = \text{const}$, where $\gamma = \frac{C_p}{C_v} = \frac{5\gamma}{3\gamma} = \frac{5}{3}$.

Because the gas is ideal (PV=nRT) it follows $TV^{\gamma-1} = \text{const} \tan t$. So

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} = (298K) \left(\frac{12.2L}{48.8L}\right)^{2/3} = 119.4K$$

$\Delta T = 119.4 - 298 = -178.6K$

$\Delta U = w = nC_v \Delta T = (5\text{moles}) \left(\frac{5\gamma}{3}\right) (-178.6K) = -11,131J$

3.2) Consider the heat engine in the diagram below which produces net work by
exploiting the temperature gradient that exists between the top of a lake and the lake
bottom. The sun sustains this temperature difference by warming the top layer of lake
water. Assume the lake has a surface area of 1.00x10^5 m^2. Assume the water at the
surface of
the lake has a temperature of 298K and the water at the bottom of the lake has a
temperature of 280K. Assume the average solar flux at the lake surface is 500 Watts m\(^{-2}\).
It is claimed that this "lake engine" can generate work at an average rate of 1.00\times10^7
Watts. Does this claim violate the First or Second Laws of Thermodynamics? Support
your answer with a calculation.

Solution: Claimed efficiency = \( \frac{10^7 \text{Watts}}{(500 \text{Watts/m}^2) \times 10^5 \text{m}^2} = 0.20 \)
Theoretical efficiency = \( \frac{298 - 280}{298} = 0.06 \)
Impossible because even though the engine conserves energy and does not violate the
First Law, the efficiency promised exceeds the efficiency limit of heat engines set by the
Second Law.

3.3) For copper metal at \( P=1 \text{atm} \) and \( T=298K \) the thermal expansivity
\( \beta = 16.5 \times 10^{-6} \text{K}^{-1} \) and the isothermal compressibility \( \kappa = 0.72 \times 10^{-6} \text{bar}^{-1} \). Calculate the
difference \( C_p - C_v \) for copper metal at \( T=298K \). The density of copper is 8920 kg m\(^{-3}\).

Solution:
\[ C_p - C_v = \frac{VT \beta^2}{\kappa} = \frac{MT \beta^2}{\rho \kappa} \]
where \( M \) is the atomic weight and \( \rho \) is the density.

From the periodic table posted in the wall of the class \( M \approx 63.6 \text{g mol}^{-1} \approx 0.0636 \text{kg mol}^{-1} \)
Then
3.4) Ammonia is a common metabolic by-product. It is also very toxic so terrestrial animals convert ammonia to urea: \( \text{NH}_2\text{CONH}_2 \). Consider the synthesis of urea from its constituent elements:

\[
C(\text{gr}) + \frac{1}{2}N_2(\text{g}) + \frac{1}{2}O_2(\text{g}) + 2H_2(\text{g}) \rightarrow \text{NH}_2\text{CONH}_2(\text{s})
\]

The table below shows entropy values at for \( T=298\text{K} \) and heat capacity values for each reaction component.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( S^0(J\text{K}^{-1}\text{mol}^{-1}) )</th>
<th>( C^0_p(J\text{K}^{-1}\text{mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(\text{gr})</td>
<td>5.69</td>
<td>8.64</td>
</tr>
<tr>
<td>N\textsubscript{2}(\text{g})</td>
<td>191.49</td>
<td>29.12</td>
</tr>
<tr>
<td>O\textsubscript{2}(\text{g})</td>
<td>205.03</td>
<td>29.36</td>
</tr>
<tr>
<td>H\textsubscript{2}(\text{g})</td>
<td>130.59</td>
<td>28.84</td>
</tr>
<tr>
<td>Urea(\text{s})</td>
<td>104.6</td>
<td>93.13</td>
</tr>
</tbody>
</table>

Calculate the entropy change for this reaction at \( T=310\text{K} \). Assume all heat capacities are constant between 298K and 310K.

\[
S(T_2) = S(T_1) + \Delta C_p \ln \left( \frac{T_2}{T_1} \right)
\]

\[
= (104.6 - 2 \times 130.59 - \frac{1}{2} \times 205.03 - 5.69 - 191.49) J\text{K}^{-1}\text{mol}^{-1}
\]

\[
+ (93.13 - 2 \times 28.84 - \frac{1}{2} \times 29.36 - 8.64 - 29.12) \ln \left( \frac{310}{298} \right) J\text{K}^{-1}\text{mol}^{-1}
\]

\[
= -456.3 J\text{K}^{-1}\text{mol}^{-1} - 16.99 \times 0.039 J\text{K}^{-1}\text{mol}^{-1} = -457.0 J\text{K}^{-1}\text{mol}^{-1}
\]

Part 4: (32 points). Perform one out of the two multi-step calculations.

4.1) Consider the formation of glucose from carbon dioxide and water, i.e. the reaction of the photosynthetic process:

\[
6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(l) \rightarrow C_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})
\]

Thermodynamic Information
<table>
<thead>
<tr>
<th></th>
<th>T=298K</th>
<th>CO₂ (g)</th>
<th>H₂O</th>
<th>C₆H₁₂O₆</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH₀</td>
<td>kJ/mole</td>
<td>-393.51</td>
<td>-285.84</td>
<td>-1274.43</td>
<td>0.0</td>
</tr>
<tr>
<td>S₀</td>
<td>J/mole-K</td>
<td>213.64</td>
<td>69.94</td>
<td>212.13</td>
<td>205.03</td>
</tr>
<tr>
<td>C_p₀</td>
<td>J/mole-K</td>
<td>37.13</td>
<td>75.30</td>
<td>218.16</td>
<td>29.36</td>
</tr>
</tbody>
</table>

Assume all heat capacities are constant between T=298K and T=330K.

a) Calculate the entropy and enthalpy changes for this chemical system at T=298K.

Solution:
\[
\Delta H^0 = 6\Delta H^0 (O_2 (g)) + \Delta H^0 (C_6H_{12}O_6 (s)) - 6\Delta H^0 (CO_2 (g)) - 6\Delta H^0 (H_2O (l))
\]
\[
= 6(0) + (-1274.45kJ) - 6(-393.51kJ) - 6(-285.84kJ) = +2801.65kJ
\]
\[
\Delta S^0 = 6S^0 (O_2 (g)) + S^0 (C_6H_{12}O_6 (s)) - 6S^0 (CO_2) - 6S^0 (H_2O (l))
\]
\[
= 6(205.03J / K) + 212.13J / K - 6(213.64J) - 6(69.94J / K) = -259J / K
\]

b) Calculate the entropy change for the surroundings at T=298K. Based on your answer is the production of glucose spontaneous at T=298? Explain.

\[
\Delta S^0_{surr} = -\frac{\Delta H^0}{T} = -\frac{2801.65kJ}{298K} = -9.40kJK^{-1}
\]

Therefore
\[
\Delta S^0_{univ} = \Delta S^0_{surr} + \Delta S^0_{rxn} = -9400JK^{-1}mol^{-1} - 259JK^{-1}mol^{-1} = -9659JK^{-1}mol^{-1}
\]
The entropy change of the universe resulting from the production of glucose and oxygen from carbon dioxide and water is negative. Assuming the universe is an isolated system, this reaction will not occur. It is not “spontaneous”.

c) Repeat the entropy and enthalpy calculations for T=330K. Does photosynthesis become spontaneous at T=330K? Explain.

d).
\[
\Delta H^0 (T) = \Delta H^0 (298K) + \Delta C_p^0 (T - 298K)
\]
\[
\Delta S^0 (T) = \Delta S^0 (298K) + \Delta C_p^0 \ln \left( \frac{T}{298K} \right)
\]
\[
\Delta C_p^0 = 6C_p^0 (O_2 (g)) + C_p^0 (C_6H_{12}O_6 (s)) - 6C_p^0 (CO_2 (g)) - 6C_p^0 (H_2O(l))
\]
\[
= 6(29.36J / K) + 218.16J / K - 6(37.13J / K) - 6(75.30J / K)
\]
\[
= 176.16J / K + 218.16J / K - 222.78J / K - 451.8J / K
\]
\[
= -280.26J / K
\]

Then…
4.2) 18 grams of water ice at 230 K are placed in thermal contact with a large heating block maintained at a temperature of 350 K. Calculate the entropy change $\Delta S$, the energy change $\Delta U$, and the enthalpy change $\Delta H$ of the water, when 18 grams of water ice at 230 K are converted to liquid water at 350 K. Also calculate the entropy change of the heating block as a result of this process and the entropy change of the universe as a result of this process. For ice $C_p=37.7 \text{ J/K}$. For liquid water $C_p=75 \text{ J/K}$. For water $\Delta H_{\text{fusion}}=6.01 \text{ kJ/mole}$. Assume the density of ice is 0.92 gm/mL and approximately constant between 230K and 273K. The density of liquid water is 1 gm/mL at 273K and approximately constant up to 350K. Assume only P-V work occurs. The external pressure is 1 atm.

Solution: Designate a three-step path from water ice at $T=230K$ to liquid water at $T=350K$:

\[
\text{ice}(230K) \rightarrow \text{water}(350K) \quad \downarrow \quad \uparrow \\
\text{ice}(273K) \rightarrow \text{water}(273K)
\]

Step 1: $\Delta H_1 = nC_{p}^{\text{ice}} \Delta T = (1\text{ mole})(37.7 \text{ J/K} \cdot \text{mole})(273K - 230K) = 1621J$

\[
\Delta S_1 = nC_{p}^{\text{ice}} \ln \left( \frac{T_{\text{final}}}{T_{\text{initial}}} \right) = (1\text{ mole})(37.7 \text{ J/K} \cdot \text{mole}) \ln \left( \frac{273}{230} \right) = 6.46J \div K
\]

\[
\Delta U_1 = q_p - P_{\text{ext}} \Delta V \approx q_p = \Delta H_1
\]

Step 2: $\Delta H_2 = (1\text{ mole})\Delta H_{\text{fusion}} = (1\text{ mole})(6010J \div \text{mole}) = 6010J$

\[
\Delta S_2 = \frac{\Delta H_2}{T_{\text{fusion}}} = \frac{6010J}{273K} = 22.0J \div K
\]

\[
\Delta U_2 = q_p - P_{\text{ext}} \Delta V \Rightarrow q_p = \Delta H_2 = 6010J; \Delta V = V_{\text{liquid}} - V_{\text{ice}}
\]

\[
\Delta V = 0.018L - (0.018L / 0.92) = -0.0016L
\]

\[
\therefore \Delta U_2 = 6010J + (-0.0016L)(1\text{ atm})(101J \div \text{L} \cdot \text{atm}) = 6010.2J
\]

Step 3: $\Delta H_3 = nC_{p}^{\text{liquid}} \Delta T = (1\text{ mole})(75J \div \text{K} \cdot \text{mole})(350K - 273K) = 5775J$
\[ \Delta S_3 = nC_p^{\text{liquid}} \ln \left( \frac{T_{\text{final}}}{T_{\text{initial}}} \right) = (1\text{ mole})(75 J / K \cdot \text{mole}) \ln \left( \frac{350}{273} \right) = 18.63 J / K \]

As before \( \Delta U_3 \approx \Delta H_3 = 5775 J \)

**Totals:**
\[ \Delta H_T^{\text{water}} = \Delta H_1 + \Delta H_2 + \Delta H_3 = 13,406 J \]
\[ \Delta S_T^{\text{water}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 47.09 J / K \]
\[ \Delta E_T^{\text{water}} \approx \Delta H_T^{\text{water}} = 13,406 J \]

**\( \Delta S \) for Surroundings:**
\[ \Delta S_{\text{surroundings}} = \frac{-\Delta H_T^{\text{water}}}{T_{\text{surroundings}}} = \frac{-13,406 J}{350 K} = -38.30 J / K \]

**\( \Delta S \) for Universe:**
\[ \Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{water}} = -38.30 J / K + 47.09 J / K = 8.79 J / K \]