Chemistry 452/456       25 July , 2005
Midterm Examination Key      Professor G. Drobny

- Universal gas constant=R=8.31J/mole-K=0.0821L-atm/mole-K
- 1 Joule=1J=1 Nt-m=1kg-m²/s²
- 101J=1 L-atm.

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.

a) Heat Capacity: Define macroscopically and also give a microscopic interpretation. Answer: The heat capacity is the change in the energy of a system per unit change in temperature $C_v = \left( \frac{\partial U}{\partial T} \right)_v$. It corresponds to a change in mechanical energy level occupation in a multi-particle system upon the absorption of heat, resulting in a change in average energy.

b) A Reversible Process: Define and indicate how this concept is relevant to physical systems. Avoid cynical responses like “it is not relevant”. Answer: A reversible process proceeds from an initial thermodynamic equilibrium to a final equilibrium through a very large number of equilibrium states. At any step the process can be reversed by the application of an infinitesimal force.

c) State Function: Define and give two examples. Answer: A property of a system that is determined solely by the equilibrium state of the system. State functions include energy $E$, enthalpy $H$, entropy $S$, free energy $A$ and $G$. When a state function changes its change is dependent only on the initial thermodynamic state and the final state.

d) Equation of State: Explain how this equation is related to the state variables. Give an example of an equation of state. Answer: A equation that relates state variables $P$, $V$, $T$, and $n$ and describes the equilibrium state of the system.

e) Exact Differential: Define using Euler’s Criterion for exactness. Explain how exact differentials are relevant to thermodynamics. Answer: A mathematical entity of the form $dZ=M(x,y)dx+N(x,y)dy$, where $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$. Integrals of exact differentials are path independent and thus differentials of state functions are exact.

f) Surface Tension: Define surface tension, describes the physical origins of surface tension and discuss how the Gibbs energy is corrected for surface tension effect. Answer: The work required to increase the surface area of a liquid by an amount $dA$ is $\delta w = \gamma dA$ where $\gamma$ is the surface tension. Surface tension results from the fact that because of intermolecular interactions within the bulk liquid, it requires work to move a molecule from the interior of liquid to the surface with fewer interactions occur. The Gibbs energy, corrected for surface tension effects, is $dG = -SdT + VdP + \sum \mu_j dn_j + \gamma dA +$
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.

a) The maximum efficiency of a steam engine can be calculated using the second law of thermodynamics. If a steam engine operates between the temperature of boiling water \( T=373 \text{K} \) and a common ambient temperature of \( T=293 \text{K} \), the efficiency is

\[
\varepsilon = \frac{373 - 293}{373} = 0.215 \text{ or } 21.5\%.
\]
Photosynthesis is a process whereby radiant energy is absorbed by plants and converted to chemical energy. This process proceeds with an estimated efficiency of 85\% even though plants do not maintain large thermal gradients. Explain how energy conversion in plants can achieve such high thermodynamic efficiencies.
Answer: Although plants do not maintain large internal thermal gradients, they are in thermal contact with the sun. In that sense the high temperature reservoir can have a very high temperature and so plants can perform photosynthesis with very high efficiencies.

b) Air is about 80\% nitrogen and 20\% oxygen, ignoring small amounts of carbon dioxide, water vapor, and trace gases. 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 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.

c) The heat capacity \( C_V \) of the monatomic gas helium at \( T=300 \text{K} \) is 12.46 J K\(^{-1}\) mole\(^{-1}\), while \( C_V \) for the diatomic gas hydrogen \( \text{H}_2 \) at \( T=300 \text{K} \) is 20.78 J K\(^{-1}\) mole\(^{-1}\). How closely do these heat capacities agree with the predictions of the equipartition principle of classical mechanics? If in either case the heat capacity data do not agree with the predictions of the equipartition principle, explain why.
Answer: The equipartition principle predicts \( C_V = \frac{3R}{2} \) for monatomic species and \( C_V = \frac{7R}{2} \) for diatomic species. But \( C_V \) for \( \text{H}_2 \) is closer to \( 5R/2 \). The discrepancy of \( R \) is due to the two vibrational degrees of freedom. Because of the large energy level spacings, vibrational levels are not thermally excited at ambient temperatures. As a result most of the population is in the ground state, and the equipartition principle does not hold for these two degrees of freedom.
d) Suppose someone claims: “I have developed a heat engine that will operate by using the temperature difference between the top and bottom waters of a lake. The engine is ultimately solar-powered because the sun sustains this temperature difference by warming the top layer of lake water. Assume the lake has a surface area of $10^5 \text{ m}^2$. 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 288K. Assume the average solar flux at the lake surface is 500 Watts/m$^2$. Based on these numbers (assumed to be truthful and valid) the engine can generate work at an average rate of $10^7$ Watts.”

Does this person’s claims for the engine’s performance violate the First Law of Thermodynamics? Does this person’s claims for engine performance violate the Second Law of Thermodynamics? Explain your answer and show relevant calculations.

Answer: This answer might require some very simply calculations. The rate of power output per unit area of lake is $10^7 \text{Watts} / 10^5 \text{ m}^2 = 100 \text{Watts} / \text{m}^2$. So the energy production does not exceed the solar flux of 500Watts/m$^2$, and energy is conserved according to the First Law. But the advertised efficiency is $100 \text{Watts} / 500 \text{Watts} = 0.2$, while the Second Law sets the theoretical limit in efficiency at $\frac{T_H - T_L}{T_H} = \frac{298 - 288}{298} = 0.034$. So the proposed engine violates the Second Law.

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

a) A major league pitcher throws a baseball with a speed of 98 miles per hour. The baseball weighs 220 grams, it travels 60 feet 6 inches from the pitcher’s mound to
home plate, and its heat capacity is 2.0 J g⁻¹ K⁻¹. Calculate the temperature rise of the ball when it is stopped by the catcher’s mitt. Assume no heat is transferred to the catcher’s mitt, or to the surrounding air. Assume also that the catcher’s arm does not recoil when he/she catches the ball. Assume constant pressure. (Note: 1 mile = 1609 meters, 1 inch = 0.0254 meters).

Solution: You have to conserve energy so the kinetic energy of the baseball has to be converted to heat when it hits the catcher’s mitt. Then

\[
\frac{1}{2}mv^2 = mC\Delta T \Rightarrow \Delta T = \frac{v^2}{2C}
\]

\[
\therefore \Delta T = \left[\frac{(98 \text{mi/hr})(1 \text{hr}/3600 \text{sec})(1609 \text{m} / \text{mi})}{2(2000 \text{J/kg} \cdot \text{K})}\right] \approx 0.480 K
\]

b) Oxygen gas reacts with solid glycylglycine $C_4H_8N_2O_3$ to form solid urea $CH_4N_2O$, carbon dioxide gas and liquid water. At T=298K and 1 atm the standard enthalpy change is $\Delta H^0_{298} = -1340.11 kJ / mole$.

\[3O_2(g) + C_4H_8N_2O_3(s) \rightarrow CH_4N_2O(s) + 3CO_2(g) + 2H_2O(l)\]

The heat capacities for the reactants and products are:
\[C_p^0(C_4H_8N_2O_3(s)) = 163.59 J / \text{mole} \cdot \text{K}; C_p^0(CH_4N_2O(s)) = 93.13 J / \text{mole} \cdot \text{K};\]
\[C_p^0(O_2(g)) = 29.36 J / \text{mole} \cdot \text{K}; C_p^0(CO_2(g)) = 37.13 J / \text{mole} \cdot \text{K}; C_p^0(H_2O(l)) = 75.30 J / \text{mole} \cdot \text{K}\]

Calculate the standard enthalpy change $\Delta H^0$ at T=330K, P = 1 atm.

Solution:
\[\Delta C_p^o = 2C_p^o(H_2O(l)) + 3C_p^o(CO_2(g)) + C_p^o(CH_4N_2O(s))\]
\[-3C_p^o(O_2(g)) + 3C_p^o(C_4H_8N_2O_3(s))]\]
\[= 103.45 J / K\]
\[\Delta H^0_{330} = \Delta H^0_{298} + \Delta C_p^0\Delta T\]
\[= (1 \text{mole})(-1340.11 kJ / mol) + (0.10345 kJ / K)(330 K - 298 K)\]
\[= -1337 kJ\]

c) d) At the summit of Mount Denali (20,320 ft) water boils at 348K. The heat of vaporization of water is 42,000J/mole and is independent of temperature between 348K and 373K. What is the atmospheric pressure at the peak of Mount Denali?

Solution:
\[
\ln \left( \frac{P_i}{P^R} \right) = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_i} - \frac{1}{T_0} \right)
\]

\[
\ln \left( \frac{P_i}{1} \right) = -\frac{42,000 \text{ J/mole}}{8.31 \text{ J/K} \cdot \text{mole}} \left( \frac{1}{348} - \frac{1}{373} \right)
\]

\[
\ln P_i = -5054K \left( 0.00287 - 0.00268 \right) K^{-1} = -0.960
\]

\[
\therefore P_i = 0.38 \text{ atm}
\]

d) Consider 0.974 moles of an ideal monatomic gas with a volume of 20L and a temperature of 500K. The gas expands adiabatically and irreversibly against a constant external pressure of 1 atm, until its pressure is also 1 atm. Calculate the final volume of the gas.

**Solution:** The expression for the final volume is obtained from the adiabatic equation

\[ w = -P_{\text{ext}} (V_2 - V_1) = nC_v (T_2 - T_1) \]

and the ideal gas law.

From the homework the final volume for an adiabatic irreversible expansion is

\[
V_2 = \frac{P_{\text{ext}} V_1 + nC_v T_1}{P_{\text{ext}} + C_v \rho_2 / R}
\]

For a monatomic ideal gas \( C_v = 3R/2 \) and \( P_2 = P_{\text{ext}} = 1 \text{ atm} \). Then

\[
V_2 = \frac{(1 \text{ atm})(20 \text{ L}) + (0.974 \text{ moles})(1.5)(0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(500 \text{ K})}{1 \text{ atm} + (1.5)(1 \text{ atm})} = 32 \text{ L}
\]

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

4.1) A thermally insulated cylinder is divided into two equal volumes by a moveable piston. See diagram below. Assume the piston is thermally insulated also. Each volume is initially 20L. The left hand chamber contains 1 mole of a monatomic ideal gas. The right hand chamber also contains 1 mole of an ideal monatomic gas. The pressure in each chamber is initially 1 atm. The gas in the left hand chamber is gradually heated until it exerts a pressure of 2 atmospheres on the piston, causing the piston to move to the right. The gas in the right hand chamber is compressed adiabatically and reversibly until its pressure is also 2 atm.

![Diagram](image)

a) Calculate the initial temperature of the gas.
Solution:

\[ PV = nRT \Rightarrow T_1 = T_1^L = T_1^R = \frac{PV_n}{nR} = \frac{(1\text{atm})(20L)}{(1\text{mole})(0.0821\text{L atm mol}^{-1}\text{K}^{-1})} = 244K \]

b) Calculate the final temperature and the final volume of the gas in the right hand chamber.

Solution: This is an adiabatic, reversible process so

\[ P_{V_1^{\gamma}} = P_{V_2^{\gamma}} \ldots \gamma = \frac{C_p}{C_V} = \frac{5}{3} \]

\[ V_2 = V_1 \left( \frac{P_1}{P_2} \right)^{\frac{1}{\gamma}} = (20L)\left( \frac{1}{2} \right)^{\frac{3}{5}} = (20L)(0.66) = 13.2L \]

\[ \therefore T_2^R = \frac{P_{V_2}}{nR} = \frac{(2\text{atm})(13.2L)}{(1\text{mole})(0.0821\text{L atm mol}^{-1}\text{K}^{-1})} = 322K \]

c) Calculate the final temperature and final volume of the gas in the left hand chamber.

Solution: The final volume is \( V_2 = 20L + 13.2L = 33.2L \). The final temperature is

\[ T_2^L = \frac{P_{V_2}}{nR} = \frac{(2\text{atm})(33.2L)}{(1\text{mole})(0.0821\text{L atm mol}^{-1}\text{K}^{-1})} = 809K \]

d) Calculate the work done in compressing the gas in the right hand chamber and the total heat \( Q \) transferred into the left hand chamber. Hint: The total heat \( Q \) that is transferred into the left hand chamber heats up the gas in the left hand chamber and results in work being done on the gas in the right hand chamber.

Solution: \( w = -nC_v(\frac{T_2^R - T_1}{2}) = (1\text{mole})\left( \frac{3R}{2} \right)(322K - 244K) = -972J \)

\[ Q = -w + nC_v(\frac{T_2^L - T_1}{2}) = 972J + (1\text{mole})\left( \frac{3R}{2} \right)(809K - 244K) = 7042J \]

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

\[ 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_12\text{O}_6(s) + 6\text{O}_2(g) \]

The following table of information will be useful in working this problem:

<table>
<thead>
<tr>
<th>T=298K</th>
<th>CO\text{2} (g)</th>
<th>H\text{2}O</th>
<th>C\text{6}H\text{12}O\text{6}</th>
<th>O\text{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_f^0 ) kJ/mol</td>
<td>-393.51</td>
<td>-285.84</td>
<td>-1274.43</td>
<td>0.0</td>
</tr>
<tr>
<td>( S_f^0 ) J/mole-K</td>
<td>213.64</td>
<td>69.94</td>
<td>212.13</td>
<td>205.03</td>
</tr>
<tr>
<td>( C_p^0 ) J/mole-K</td>
<td>37.13</td>
<td>75.30</td>
<td>218.16</td>
<td>29.36</td>
</tr>
</tbody>
</table>

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

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

b) Calculate the free energy change at T=298K. Based on your answer is the production of glucose spontaneous at T=298? Explain.
\[
\Delta G^0 = \Delta H^0 - T\Delta S^0 = 2801.65kJ - (298K)(-259kJ/K) \\
= 2879kJ \Rightarrow \Delta G^0 > 0 \\
so the reaction is not spontaneous.
\]
c) Repeat the entropy and enthalpy calculations for T=330K. Assume all heat capacities are independent of temperature between 298K and 330K.
\[
\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 = 6\Delta C_p^0_f(O_2(g)) + \Delta C_p^0_f(C_6H_{12}O_6(s)) - 6\Delta C_p^0_f(CO_2(g)) - 6\Delta C_p^0_f(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... \\
\Delta H^0(T) = \Delta H^0(298K) + \Delta C_p^0(T-298K) = 2801000J + (-280.26J/K)(330K - 298K) = 2792.03kJ \\
\Delta S^0(T) = \Delta S^0(298K) + \Delta C_p^0 \ln \left( \frac{T}{298K} \right) = -259J/K + (-280.26J/K)\ln \left( \frac{330K}{298K} \right) = -287.49J/K \\
\Delta G^0 = \Delta H^0 - T\Delta S^0 = 2792000J - (330K)(-287.49J/K) = 2886.87kJ \\
d) Is the free energy change for glucose production via photosynthesis increasing or decreasing as the temperature increases? Explain.

The reaction at T=330K has a free energy change that is even more positive...because the entropy change has become more negative.