

20.110/5.60/2.772 Fall 2005
Homework #2
Due Friday September 23

1. **True or False.** Give a brief explanation for each and if false provide a counter example:

- (a) The enthalpy of a system is always greater than its internal energy.
- (b) In the reversible isothermal expansion of a real gas, the energy remains constant.
- (c) In the reversible adiabatic expansion of a real gas, the enthalpy always decreases.
- (d) At a given temperature and volume, the pressure of one mole of a real gas is always less than the pressure of one mole of an ideal gas.
- (e) The work done by a gas in an irreversible expansion from state 1 to state 2 is always less than the work done by a gas in a reversible expansion from state 1 to state 2.

2. **State Functions:** An ideal monotonic gas is initially at the following conditions: $V = 0.5L$, $p = 1\text{bar}$, $T = 298\text{K}$ (State 0). It is subjected to the following cycle, where each step between states is reversible:

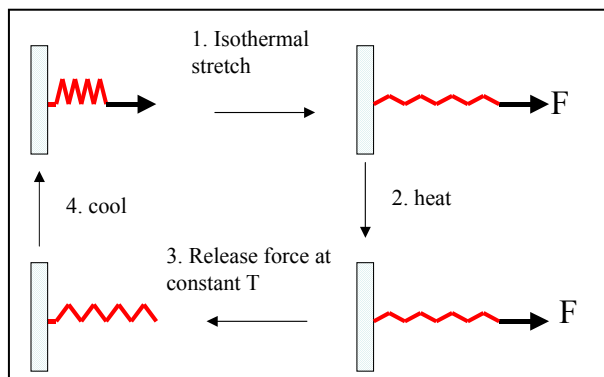
- Step 1: Isothermal expansion to 1 L (State 1)
- Step 2: Adiabatic expansion to 1.5 L (State 2)
- Step 3: Isothermal compression to 0.75 L (State 3)
- Step 4: Adiabatic compression to 0.5 L (State 0)

Calculate the heat, work, and change in internal energy for the gas at each step. For one complete round of the cycle, what is the net value of q ? the net value of w ? the net value of ΔU ?

3. **State Functions:** The thermo-mechanical properties of certain proteins play an important role in response of cells to perturbations in the mechanical environment and to other forms of stress. A protein derived from the supporting skeleton of the red cell membrane is subjected to the following cycle conducted at constant pressure, starting from State 0, where the protein is in an unstressed state at $T = 298\text{K}$.

Step 1. Protein is stretched 20 nm at constant T in a reversible process. The protein spring constant is 1 mN/m.

Step 2. The protein is heated 20°C to 318 K while held stretched (no additional extension). For the stretched protein $C_p = 30,000\text{ J/K-mol}$ ($5 \times 10^{-20}\text{ J/K-molecule}$) and is approximately constant over the temperature range.

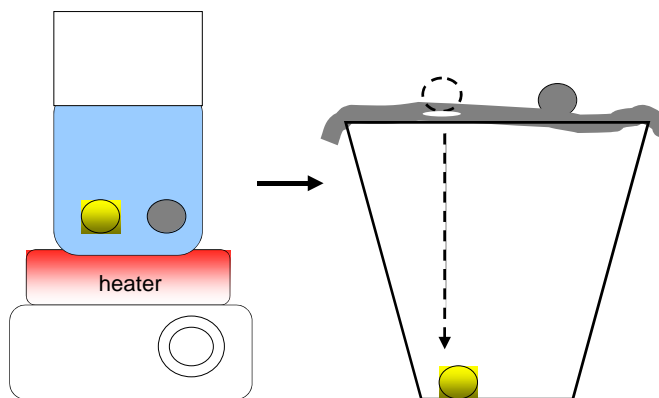


Step 3. The force is released while the temperature is held constant, and the protein relaxes to a random coil configuration characteristic of a thermally-denatured protein. The enthalpy change associated with the process is -6×10^{-19} J.

Step 4. The protein is cooled back to 298 K and undergoes a refolding process. The enthalpy change associated with this process is -9×10^{-19} J.

What is the enthalpy change associated with the first step? What is the change in internal energy? You may assume that there are no volume changes associated with this constant pressure cycle.

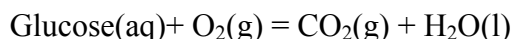
- 4. The Mystery of the Melting Wax.** Two metal balls, one gold and one aluminum (1 mole of each), both initially at a temperature of 25°C , are placed in a beaker of water on a hot plate and allowed to equilibrate at 100°C (the temperature of the heat bath)- step (i). The two marbles are then removed and placed immediately onto two different strips of wax (1 mole of wax each, the wax is initially at room temperature) stretched over a can (illustrated below). The Au ball melts through the wax strip and falls into the can, while the Al marble remains on the wax without melting it (step (ii)). All of these processes are occurring at a constant pressure of 1 atm. What's going on here? Let's explain it step by step. The heat capacities of the wax and two metals are approximately constant over the temperature ranges of interest. Note that the thermal conductivity of both metals is very high- the observed result is not occurring due to a difference in the kinetics of heat transfer. The Al marble will *never* melt through the wax!



- What heat transfers are occurring in the described processes? (qualitatively).
- Write equations that would allow you to quantitatively calculate the heat transferred into the Au marble and the heat transferred into the Al marble for step (i). What information must you be given to finish the calculation? Will the heat transferred to the Au marble equal the heat transferred to the Al marble?
- Assume whatever heat that leaves the Al marble in step (ii) enters the wax strip it sits on (none is lost to the surroundings). According to the zeroth law, the Al marble and wax strip will have the same final temperature at equilibrium. Write an expression for the final temperature T_f of the Al marble and wax strip as a function of their molar heat capacities, \bar{C}_p^{Al} and \bar{C}_p^{wax} .
- Make a hypothesis that explains the end result in step (ii).

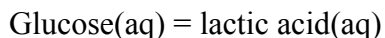
5. The thermochemistry of respiration in humans. Given below is tabulated data on the enthalpies of formation and heat capacities for several compounds at 298 K. Assume the heat capacities are approximately constant over the temperature ranges of interest.

- e. Aerobic respiration culminates in the conversion of glucose and oxygen into CO₂, water, and energy:



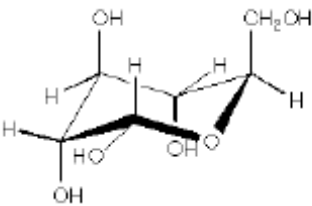
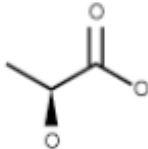
How much heat is liberated per mole of reaction at 298 K?

- f. Anaerobic respiration in humans takes over in conditions where oxygen is limiting. The metabolic pathway leads to the conversion of glucose to lactic acid:



How much heat is liberated per mole of the anaerobic reaction at 298 K? What is the ratio aerobic: anaerobic of enthalpies produced per mole of glucose by the two pathways?

- g. In vivo, these reactions of course occur at the physiological temperature of 37°C. Using the data from the table below, calculate the enthalpy change per mole for the reaction of part (a) as it occurs at 37°C. (Assume \bar{C}_p 's are independent of temperature in this temperature range.)

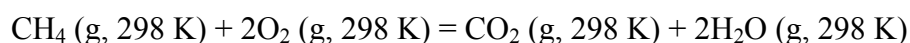
Compound	ΔH_f° (kJ/mole) (at 298 K, 1 atm, pH 7, 0.25M ionic strength, for aq species)	\bar{C}_p (J/mole K)
Glucose (aq) (C ₆ H ₁₂ O ₆) 	-1267.11	210
O ₂ (g)	0	29.4
CO ₂ (g)	-393.51	37.1
H ₂ O (l)	-285.77	75.3
Lactic acid (aq) (lactate) 	-688.28	-

6. Thermochemistry

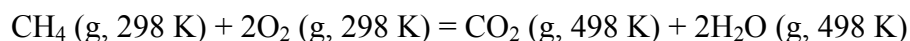
Consider the following data

	$\Delta\bar{H}_f^\circ (kJ \cdot mol^{-1})$	$\bar{C}_p (J \cdot K^{-1} \cdot mol^{-1})$
CO ₂ (g)	-393.5	37
H ₂ O (g)	-241.8	33
CH ₄ (g)	-74.9	35
N ₂ (g)	0	29
H ₂ O (l)	-285.9	75

- (a) Calculate ΔH for the following isothermal change in state at 298 K and 1 bar.



- (b) Calculate ΔH for the following non-isothermal change in state at 1 bar. (Assume all C_p 's to be independent of temperature. Careful with the units!).



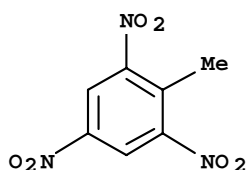
- (c) In a type of water heater, a flame of methane, (CH₄), heats a container containing liquid water. Assume that 1.0 mole of CH₄ and 10 moles of air (2 moles of O₂ and 8 moles of N₂) are used during the heating process. Assume also that complete oxidation of CH₄(g) to CO₂(g) and H₂O(g) occurs. Assume that all the gases, including N₂ (g) from the air, enter the heater at 298 K and leave at 498 K.

- (i) Write the change in state involving all the gases that enter and leave the heater (CH₄, O₂, N₂, CO₂, H₂O).

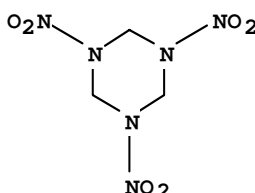
- (ii) Calculate ΔH for this change in state

- (iii) Assume that all the heat generated by the methane flame during the process is transferred to 3.5 liters (195 moles) of liquid water. Assume that the combustion is done under a constant pressure of 1 bar. If the water was initially at $T = 298 \text{ K}$, calculate the temperature of the water at the end of the process. (Careful with the units!)

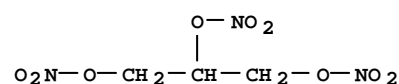
7. Thermochemistry. Explosive compounds are molecules (or materials) in which the oxidizer and the fuel are contained in the same molecule. This leads to a rapid, highly exothermic, self-sustaining reaction, which results in large increases in pressure and temperature (i.e. a shock wave). Examples of explosives that are in common use are TNT, RDX, and nitroglycerine (NG).



TNT
 $\text{C}_7\text{H}_5(\text{NO}_2)_3$
 MW = 227



RDX
 $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$
 MW = 222

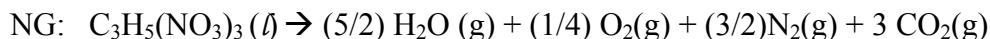
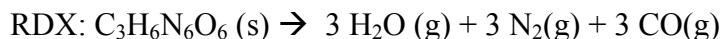
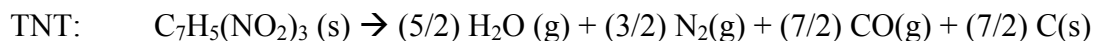


NG
 $\text{C}_3\text{H}_5(\text{NO}_3)_3$
 MW = 227

Heats of formation for these compounds are:

$$\Delta H_f^\circ (\text{TNT}) = -35.5 \text{ kJ/mole} \quad \Delta H_f^\circ (\text{RDX}) = +61.5 \text{ kJ/mole} \quad \Delta H_f^\circ (\text{NG}) = -354.4 \text{ kJ/mole}$$

(a) Calculate the heats of explosion for each of these materials, that is, the enthalpy change when each undergoes spontaneous decomposition to stable gaseous products. Assume that the balanced reactions that take place are:

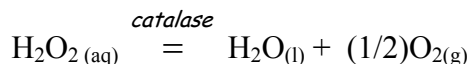


Assume that all species are at $p = 1 \text{ bar}$ and $T = 25^\circ \text{ C}$ (298 K). Actual explosions produce complex mixtures of products at high transient p and T but that calculation gets much too complicated. Use enthalpy values for H_2O , CO , CO_2 , NO , etc. given in Appendix C of SAB. For the excess $\text{C}(\text{s})$ soot produced in a TNT explosion, use the value for elemental $\text{C}(\text{graphite})$.

(b) Which of these compounds would yield the highest specific blast energy, that is $\Delta H_{\text{explosion}}$ per kilogram of material?

(c) Your answer to (b) may in fact not be the most suitable material to use in a portable explosive device. Can you think of a reason why?

8. **Calorimetry.** An aqueous solution of unoxygenated hemoglobin containing 5.00 g of protein ($M \approx 64,000 \text{ g mol}^{-1}$) in 100 cm^3 of solution is placed in an insulated vessel. When enough molecular oxygen is added to the solution to completely saturate the hemoglobin, the temperature rises 0.031°C . Each mole of hemoglobin binds exactly 4 moles of oxygen. What is the enthalpy of reaction per mole of oxygen bound? The heat capacity of the solution may be assumed to be $4.18 \text{ J K}^{-1} \text{ cm}^{-3}$.
9. **Calorimetry.** The enzyme catalase catalyses the decomposition of hydrogen peroxide by the following endothermic reaction:



Estimate the minimum detectable concentration of hydrogen peroxide if a small amount of catalase (solid) is added to 1L of a hydrogen peroxide solution in a calorimeter at 298 K. Assume that the temperature rise of 0.02°C can be distinguished. The specific heat capacity of the hydrogen peroxide solution is a constant: $4.18 \text{ kJ K}^{-1} \text{ kg}^{-1}$. The standard enthalpy of formation of hydrogen peroxide is -191.7 kJ/mole , and the standard enthalpies of formation of water and oxygen were provided in problem 3.

(2-23 p. 64 Tinoco, Sauer, and Wang, *Physical Chemistry: Principles and Applications in Biological Sciences*, 3rd ed., Prentice-Hall, Englewood Cliffs, New Jersey (1995))

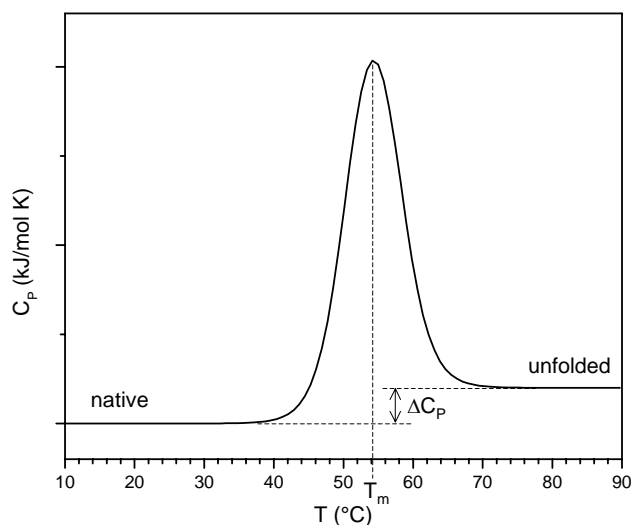
10. Differential Scanning Calorimetry.

Proteins unfold from their native (folded) state to a denatured (unfolded) state around a temperature T_m (called the melting temperature). The unfolding process requires an input of heat ($\Delta H_{\text{unfolding}} > 0$).

native = unfolded

A Differential Scanning Calorimeter (DSC) is an instrument which measures the heat absorption of a sample as a function of temperature. A solution of a protein and a reference solution (solvent only) are placed in an insulated chamber at constant pressure. The samples are heated so that the temperatures increase at a constant rate of $1^\circ\text{C}/\text{min}$. When the protein sample undergoes the transition from native to unfolded, some of the heat is used to drive the unfolding instead of raising the temperature. The instrument varies the applied power to the protein sample so that the two cells are maintained at the same temperature. The experiment measures the heat transferred into the solutions per unit time. Since $dq = C_p dT$, and dT is constant per unit time by design, the experiment measures an apparent C_p . Consequently the protein solution effectively experiences a sharp increase in apparent heat capacity C_p (see figure) during the transition. The applied power (in $\text{J}/(\text{K min})$) as a function of temperature can be converted to the C_p of the protein sample ($\text{J}/(\text{K mol})$) if the molecular weight and protein concentration is known.

The change in C_p upon unfolding, ΔC_p , is the difference in the baselines before and after the transition. The midpoint of the peak is the melting temperature, T_m .



a) DSC data allows one to obtain ΔH for the unfolding of the protein, $\Delta H_{\text{unfolding}}$. Sketch in the figure, or describe in words or in a mathematical relation how you would obtain $\Delta H_{\text{unfolding}}$ from information obtained in a DSC experiment.

b) The unfolding temperature, T_m , for a protein can be changed by varying pH or other solvent conditions. The protein cytochrome c is measured to have $\Delta H_{\text{unfolding}} = 368$ kJ/mol at 70 °C and $\Delta H_{\text{unfolding}} = 210$ kJ/mol at 50 °C. Calculate ΔC_p ($C_{p,\text{unfolded}} - C_{p,\text{native}}$) for cytochrome c, assuming ΔC_p is constant over this temperature range. (from Eisenberg and Crothers 2.23)

Additional Practice Problems (not graded):

1. When propane gas (C_3H_8) is mixed with air and burned, the products are $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and unreacted $\text{N}_2(\text{g})$. Assume air is a mixture of N_2 and O_2 in a 4 to 1 molar ratio. Assume also that the flame burns under adiabatic and constant pressure conditions. You are also given that the standard heat of formation, ΔH_f° and heat capacity C_p for $\text{C}_3\text{H}_8(\text{g})$ at 298.15 K are -104.00 kJ mol $^{-1}$ and 84.00 J K $^{-1}$ mol $^{-1}$. Other necessary heats of formation and heat capacities are given in table C.2 of the textbook.

(a) Write the change in state that occurs when 1.00 mole of $\text{C}_3\text{H}_8(\text{g})$ and a stoichiometric amount of air (i.e. containing just enough O_2 to completely burn propane) react adiabatically.

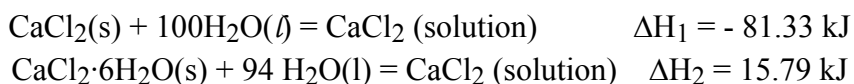
(b) Calculate the standard enthalpy change for the isothermal combustion of propane at 298.15 K.

(c) Assume all the gases are ideal. Then $\Delta H^\circ(298.15 \text{ K})$ from part (b) will correspond to the isothermal ΔH for this reaction at the actual partial pressures in the air-propane mixture. Assume that all the C_p 's are independent of T , and calculate the final temperature for the adiabatic flame.

2. The enthalpy of hydration of CaCl_2



cannot be measured because of the slow kinetics of the reaction in the solid state. However the heats of solution of $\text{CaCl}_2(\text{s})$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$ can be measured at 298.15 K:



- Calculate the enthalpy of hydration, $\Delta\text{H}(\text{hydration})$.
- Estimate the amount of anhydrous $\text{CaCl}_2(\text{s})$ in kg which would be required to completely melt a layer of ice 1 mm thick on a sidewalk 1 m wide by 10 m long, assuming that all the heat is provided by hydration of $\text{CaCl}_2(\text{s})$. The $\Delta\text{H}_{\text{fusion}}$ (heat of melting) of water is 6 kJ/mole.

3. A variety of solid and liquid fuels are used today to provide energy. These include:

- petroleum-derived hydrocarbons, typically alkanes with composition $\text{C}_n\text{H}_{2n+2}$
- coal, which contains approximately equimolar amounts of carbon and hydrogen
- biomass derived fuels which are typically cellulose, i.e. carbohydrate based
- ethanol is also used as an automotive fuel under certain circumstances

For each of these four types of fuels, calculate the energy available per kg of fuel assuming complete combustion to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, First write a balanced stoichiometric equation for the combustion reaction for each of the following model compounds (all at 298 K):

for petroleum based fuel:	hexane, $\text{C}_6\text{H}_{14}(\text{g})$	$\Delta\text{H}_f^\circ = -167 \text{ kJ/mole}$
for coal:	benzene, $\text{C}_6\text{H}_6(\text{g})$	$\Delta\text{H}_f^\circ = +83 \text{ kJ/mole}$
for biomass derived fuel:	glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	$\Delta\text{H}_f^\circ = -1260 \text{ kJ/mole}$
ethanol:	$\text{C}_2\text{H}_5\text{OH}(\text{g})$	$\Delta\text{H}_f^\circ = -235 \text{ kJ/mole}$

Then calculate ΔH per mole for the combustion reaction and calculate $\Delta\text{H}/\text{kg}$ of fuel.

Rank these four types of fuel in order of energy per kg of fuel, from highest to lowest. Are there considerations that would make it desirable to use a lower-energy form of fuel in some situations?

4. One gram of liquid benzene is burned in a bomb calorimeter. The temperature before ignition was 20.826 °C, and the temperature after the combustion was 25.000 °C. This was an adiabatic calorimeter. The heat capacity of the bomb, the water around it, and the contents of the bomb before the combustion was 10,000.0 J K⁻¹. Calculate ΔH_f° for $\text{C}_6\text{H}_6(\text{l})$ at 298.15 K from these data. Assume that the water produced in the combustion is in the liquid state and the carbon dioxide produced in the combustion is in the gas state.