

20.110/5.60/2.772 Fall 2005
Homework #1
Due Friday September 16

1. Identifying boundary conditions.

Classify the thermodynamic systems described below as open, closed, or isolated:

- The system is a suspension of cells in culture media contained in a covered plastic Petri dish; the surroundings: the dish is sitting within an incubator which maintains a constant temperature of 37°C and provides CO₂ gas to the incubator chamber at a constant level of 5 volume %.
- The system is a cell and its surroundings are the culture medium in which it is suspended. The medium is maintained at a constant temperature of 37°C.
- The system is a solution contained in a sealed, thermally insulated flask.
- The system is a fertilized chicken egg in a constant-temperature incubator
- A system that exchanges no heat with its surroundings is called *adiabatic*. Could an open system also be adiabatic? Could an adiabatic system also be closed? Explain your answers.

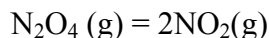
2. Equations of State. (from SAB)

A mole of n-hexane is confined in a volume of 0.5 L at 600 K. What will be the pressure according to:

- the ideal gas law?
- the van der Waals equation of state? For n-hexane, $T_c = 507.7$ K and $P_c = 30.3$ bar.
- the van der Waals equation of state correctly predicts the pressure for real n-hexane- what factors are accounted for by the van der Waals equation of state, which are missing from the ideal gas law?

3. Chemical Equilibrium of Ideal Gases.

Nitrogen tetroxide is partially dissociated in the gas phase according to the reaction



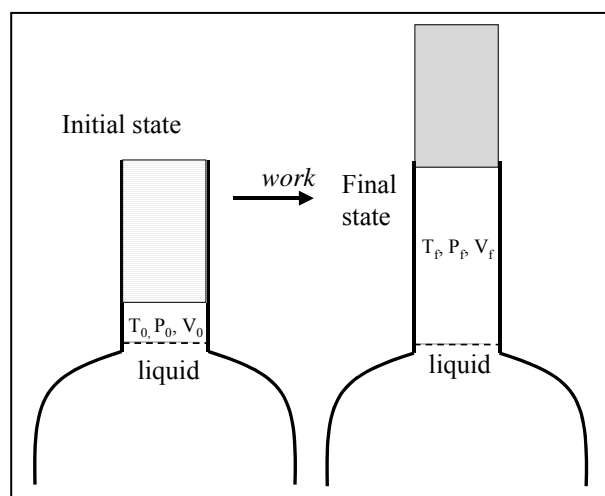
A mass of 1.588 g of N₂O₄ is placed in a 500 cm³ glass vessel at 298 K and dissociates to an equilibrium mixture at 1.0133 bar. (1) What are the mole fractions of N₂O₄ and NO₂? (b) What percentage of the N₂O₄ has dissociated. Assume that the gases are ideal.

4. First Law Use Applied to Ideal Gases.

A beverage is contained in a corked bottle. A small amount of gas is present in the gap between the liquid and the cork in the neck of the bottle so that the distance between the top of the liquid and the bottom of the cork is 1 cm and $V_0 = 2.5\text{cm}^3$. The top of the cork (Area = 2.5 cm²) is initially flush with the top of the bottle. Depending on the value of P_0 relative to P_{atm} , the gas may do work or the system (i.e., the person who wants the cork out) may do work in moving the cork to final position where it is just ready to leave the bottle. For the calculations below, assume that the cork is frictionless and that the change in potential energy of the cork is negligible (i.e., assume the cork has no mass). The external pressure is constant at 1 atm and the ambient temperature is 300K. You may assume the gases are ideal.

(a) In the first case, the beverage was fermented in the bottle, generating 6 atm pressure from production of CO₂. If $V_f = 2.5 V_0$, what is the final pressure if the process is isothermal? What is the change in internal energy of the gas during the process?

(b) Different operators employ different methods of cork removal for the situation in part a. The cork is initially held in place by a wire mesh. Consider two cases – one where the mesh is removed and no attempt is made by the operator to restrain the cork, in which case it moves quite suddenly to the “final” position (and then likely pops off to hit the ceiling, though that aspect is not part of this problem), and a second where the operator places a restraining force (e.g., a hand) against the cork and lessens the force infinitely slowly. Calculate the work done in each case. Is the work positive or negative from the point of view of the operator? How much heat enters or leaves the gas during the process?



(c) Repeat part b for case 2 (slow, controlled removal) but now consider that the process occurs adiabatically rather than isothermally. The heat capacity of CO₂ is 37 J/mol-K. What is the final temperature of the gas? Does it seem realistic that the process is close to the pure adiabatic limit?

(d) Compare the work done in part a and b with the work required to lift a glass of liquid weighing 0.25 kg a distance of 0.2 m.

(e) Now consider a different beverage that is not fermented in the bottle. The initial pressure in the head space is 1 atm and $V_f = 6V_0$. Calculate the work involved in moving the cork from the initial to the final position if the process is isothermal and the force put on the cork is increased slowly (i.e., process is reversible).

5. **Mathematical Manipulation of State Functions.** (from SAB)

The cubic expansion coefficient is defined as

$$\alpha = 1/V (\partial V/\partial T)_P$$

and the isothermal compressibility by

$$\kappa = -1/V (\partial V/\partial P)_T$$

- Calculate these quantities for an ideal gas
- Write an equation of state for a liquid for which α and κ are constant?

6. **Surface tension and the work to create new surfaces.**

(a)(from SAB) The surface tension of water is $71.97 \times 10^{-3} \text{ N m}^{-1}$ or $71.97 \times 10^{-3} \text{ J m}^{-2}$ at 25°C. Calculate the surface energy in Joules of 1 mole of water dispersed as a mist containing droplets of $1 \mu\text{m}$ (10^{-4} cm) in radius. The density of water may be taken as 1.00 g cm^{-3} .

(b) Molecules having both regions that are hydrophobic (‘water-hating’) and others that are hydrophilic (‘water-loving’) are known as amphiphiles. A common class of amphiphiles are

surfactants (in everyday experience, soaps), which typically have a nonpolar alkyl chain attached to a charged and/or polar headgroup. Surfactants are so named because they tend to localize at surfaces and interfaces formed between polar liquids (e.g., water) and nonpolar liquids (oils)/free surfaces (e.g., a water/air interface). The presence of a surfactant at an interface can dramatically change the thermodynamic properties of a system. The surface tension of water containing 0.05 mg/mL SDS is $60.5 \times 10^{-3} \text{ mN m}^{-1}$.

- i. Consider a film of water being spread across a wire frame as shown in SAB Fig 2.10. The y (vertical) dimension of the frame is 5 cm while the initial x dimension of the film is 4 cm. Calculate the work required to move the bar at the left end of the film 1 cm if the film is formed from pure water.
- ii. How much more (or less) work is required to move the bar the same distance if the film is formed from a solution of SDS in water?

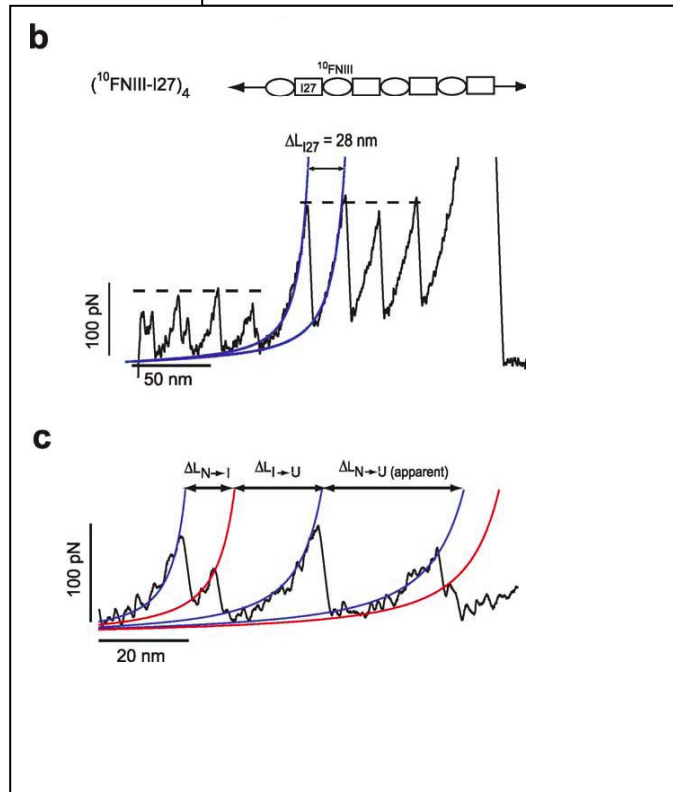
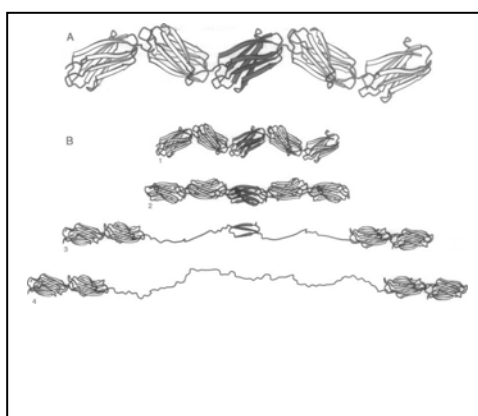
7. **Work in stretching an extracellular matrix protein.**

The extracellular matrix protein fibronectin is nearly ubiquitous in the body. Fibronectin is a large (450 Kda) dimer composed of homologous, repeating structural motifs (classified as fibronectin repeats FN-I, FN-II, and FN-III) that are grouped together into functional domains (see <http://www.ks.uiuc.edu/Research/fibronectin/>).

Cells have specific surface receptors (integrins) that bind to fibronectin, and they can migrate through gels or across substrates that contain fibronectin. Cells pull on fibronectin in the matrix and can deform it, and there is much speculation on the role of the

mechanical properties of fibronectin in determining how cells respond to a matrix that contains fibronectin. Many efforts are underway to reproduce properties of fibronectin in synthetic polymers used in tissue engineering. For a movie of fibronectin being stretched by cells in real time see the class web site link to <http://www.pnas.org/cgi/content/full/96/5/2153/DC1>.

An example of how contiguous domains of fibronectin might unfold is shown in the figure [from Erickson HP. Reversible unfolding of fibronectin type III and immunoglobulin domains provides the structural basis for stretch and elasticity of titin and fibronectin. Proc Natl Acad Sci U S A. 1994 Oct 11;91(21):10114-8]. The diagram labeled A in the figure shows five domains of fibronectin, and B shows a time sequence of the molecule being stretched causing rupture and unraveling of the central domain. Although not shown, continued stretching would unravel additional domains.



The nature of mechanical unfolding and the forces involved can be followed using single force measurements, where the molecule is attached at one end to a surface and the other end is pulled with a tiny cantilever sensitive to forces in the pN range. Fernandez and colleagues have used this method to investigate the stability of different domains within FN, and to parse the roles of specific bonds using site-directed mutagenesis [see Li L, Huang HH, Badilla CL, Fernandez JM. Mechanical unfolding intermediates observed by single-molecule force spectroscopy in a fibronectin type III module. J Mol Biol. 2005 Jan 28;345(4):817-26]. The figure to the right shows two separate experiments with force magnitude shown on the y-axis and the length the molecule is extended from its original state is shown on the x-axis. Focusing on the trace shown in figure c, the force required to stretch the molecule increases from 0 up to ~90 pN as the molecule extends 18 nm; a domain then ruptures and the force required for extension decreases, then rises again as the next domain is stretched. The rupture of each domain leads to a peak in the force-extension curve.

(a) For the force-extension curve shown in figure c, estimate the work required to extend the molecule 20 nm beyond its initial state (i.e., the work associated with the first peak). Use a diagram to illustrate your method. Please report the work done on fibronectin as positive and that done by fibronectin as negative.

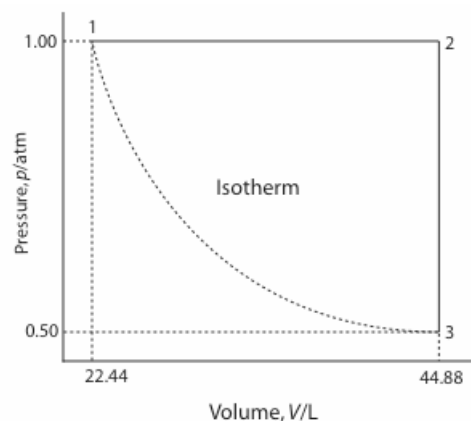
(b) Compare the work you calculate in part a to the work required if fibronectin acts as a simple spring with a spring constant of 50 mN/m (Li F, Redick SD, Erickson HP, Moy VT. Force measurements of the alpha5beta1 integrin-fibronectin interaction. Biophys J. 2003 Feb;84(2 Pt 1):1252-62.) For a simple spring, the force exerted *by the spring* in response to perturbation is $F_s = -k(x - x_0)$ where k is the spring constant (in units of F/length) and x_0 is the unstressed position of the spring (the + x direction corresponds to stretching the spring). In figure c, " $x - x_0$ " corresponds to the magnitude of the displacement (plotted on the x-axis), and the force (y-axis) is the force exerted by the probe (i.e., opposite in sign to the force of the spring). Using the value of the work you calculated in part a, estimate the spring constant for fibronectin (you will need to derive an analytical expression relating the spring constant to work, starting with the definition of F_s above). Do you get 50mN/m? Does the shape of the force-displacement curve provide insight into why your answer might be different?

8. **First Law, work, heat.**

A sample consisting of 1 mole of a monatomic ideal gas (for which $\bar{C}_V = \frac{3}{2}R$) is taken through

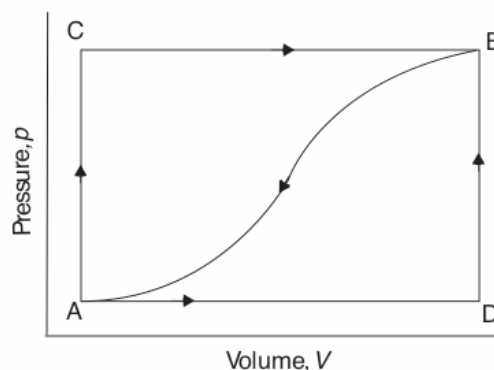
the path (solid line) shown in the figure at right.

(a) Determine the temperature at 1, 2, and 3. (b) Calculate q , w , ΔU and ΔH for each step and for the overall path. If a numerical answer cannot be obtained from the information given, then write in + (positive), - (negative), or ? (can't tell) as appropriate.



9. **First Law and Path Dependence of Work and Heat.**

When a system is taken from state A to state B along the path ACB in the figure at right, 80 J of heat flows into the system and the system does 30 J of work. (a) How much heat flows into the system along path ADB if the work done is 10J? (b) When the system is returned from state B to A along the curved path, the work done on the system is 20J. Does the system absorb or liberate heat, and how much? (c) If $U_D - U_A = +40\text{J}$, find the heat absorbed in the processes AD and DB.



10. **First law and Equivalence of Work and Heat.**

You want to heat 1 kg of water 10°C , and you have the following four methods under consideration. The heat capacity of water is $4.184 \text{ J K}^{-1} \text{ g}^{-1}$.

- You can heat it with a mechanical eggbeater that is powered by a 1-kg mass on a rope over a pulley. How far does the mass have to descend in the earth's gravitational field to supply enough work?
- You can send 1 A through a $100\text{-}\Omega$ resistor. How long will it take?
- You can send the water through a solar collector that has an area of 1 m^2 . How long will it take if the sun's intensity on the collector is a $4 \text{ J cm}^{-2} \text{ min}^{-1}$?
- You can make a charcoal fire. The heat of combustion of graphite is -393 kJ mol^{-1} . That is, 12 g of graphite will produce 393 kJ of heat when it is burned to $\text{CO}_2(\text{g})$ at constant pressure. How much charcoal will have to burn?

Additional Practice Problems (not graded):

- 6.0 moles of molecular hydrogen are contained in a 1.0 L cylinder at 30°C . Calculate the pressure in bar according to:
 - the ideal gas law
 - the van der Waals equation. The van der Waals constants for H_2 are $a = 0.2476 \text{ L}^2 \text{ bar mol}^{-2}$ and $b = 0.02661 \text{ L mol}^{-1}$. Assuming that the van der Waals equation gives the right answer, what is the percent error in using the ideal gas law?
- Two moles of an ideal gas initially at 50°C and 10 bar are expanded isothermally and reversibly to a final volume of 30 L. Calculate the final pressure, the heat, the work and ΔU in the change of state.
 - Two moles of an ideal gas initially at 50°C and 10 bar are expanded isothermally against vacuum (external pressure of 0 bar) to a final volume of 30 L. Calculate the final pressure, the heat, the work and ΔU in the change of state.

- (c) Two moles of an ideal gas initially at 50 °C and 10 bar are expanded isothermally against a pressure of 1 bar to a final volume of 30 L. Calculate the final pressure, the heat, the work and ΔU in the change of state.
3. A chemical reaction takes place in a container of cross-sectional area 50.0 cm². As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system. (Assume all gases are ideal).
4. In the isothermal reversible compression of 1.77 mmol of an ideal gas at 273 K, the volume of the gas is reduced to 0.224 of its initial value. Calculate w for this process.
5. A 5.0 g block of solid carbon dioxide is allowed to evaporate in a vessel of volume 100 cm³ maintained at 25°C. Calculate the work done when the system expands (a) isothermally against a pressure of 1.0 atm, and (b) isothermally and reversibly to the same volume as in (a). (Assume all gases are ideal).
6. Show that the differential of df is inexact.

$$df = dx - \frac{x}{y} dy$$

Thus, the integral $\int df$ depends on the path. However, we can define a new function g by

$$dg = \frac{1}{y} df$$

which has the property that dg is exact. Show that dg is exact, so that

$$\oint dg = 0$$

7. The internal energy change, ΔU , for the conversion of 1 mole of Compound A to Compound B is +0.2 kJ. Both A and B are solids with densities of 2.5 and 3.0 g/cm³, respectively.
- (a) Calculate the difference between enthalpy and internal energy when the pressure is 1 bar.
- (b) Perform the calculation again when the pressure is raised to 100 bar.
- (c) Under what circumstances is it reasonable to assume that ΔU and ΔH are identical?