Name key

MCB C100A / Chem C130

Midterm 2

Spring 2008

5 pages total including cover

POSSIBLY USEFUL INFORMATION:

R = 8.314 J/mol/K = 1.987 cal/mol/K = 0.082 L atm/K
$k_B = 1.38 \times 10^{-23}$ J/K
N_A (Avagadro's number) = 6.02×10^{23}

properties of water:

	ice	liquid water	water vapor
C_p	2.1 J/K/g	4.2 J/K/g	1.8 J/K/g

density of ice: 0.95 g/ml of water 1.00 g/ml of water vapor (at 1 atm) 8×10^{-4} g/ml
heat of melting of ice 333 J/g
heat of vaporization of water 2216 J/g

Problem 1.

Consider a system comprised of two standard six sided dice, one red and one blue (distinguishable).

a) When the two dice are rolled, what is the probability that the red one is a four?

six faces could come up, one is a four $= \frac{1}{6}$
independent of blue die

b) What is the probability that the red one is a four and the blue one is a three?

prob red = 4 is $\frac{1}{6}$
prob blue = 3 is $\frac{1}{6}$

$P_{total} = P(red\,4) \times P(blue\,3) = \frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$

c) What is the multiplicity of the result that the sum of the numbers on the two dice is seven?

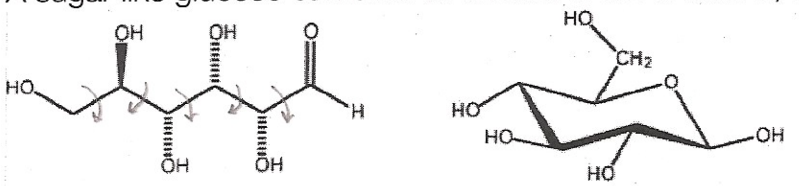
How many combinations give seven?

red	1	2	3	4	5	6
blue	6	5	4	3	2	1

$\Rightarrow$ multiplicity is 6

Problem 2.

A sugar like glucose can exist as a linear chain of atoms, or as a closed ring:



Assume that there are three low energy rotamers (conformational states) for the carbon-carbon bonds (ignore hydrogens) in the linear form, and the defined geometry shown for the closed form:

a) calulate the conformational entropy arising from bond rotations for the linear form (give a numerical result per mole of glucose).

5 single bonds, 3 conformers each (independent) so

$W_{lin} = 3^5$ conformers $\quad S = R \ln W_{lin} = 8.314 \times \ln(3^5) = 46\ J/mol/K$
(per mole)

b) estimate the contribution of conformational entropy to the reaction of the linear chain going to the closed cyclic form.

cyclic form has 1 conformer $\quad S = R \ln W_{cyc} = 0$

$\Delta S = R \ln W_{cyc} - R \ln W_{lin} = -46\ J/mol/K$

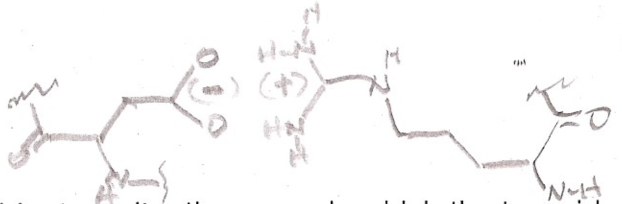
c) experimentally it is found that for glucose in solution only about 0.1% is in the linear form, is this consistent what you would predict from the answer in **b)**? (discuss briefly) NO.

Observation means that closing must be favorable, negative ΔG, but $\Delta G = \Delta H - T\Delta S$, and $-T\Delta S = +14\ kJ/mol$

The entropy change in the reaction is unfavorable, neg. ΔG must come from neg. ΔH.

Problem 3.

a) Name two amino acids which could form a salt bridge together that could stabilize a protein structure at neutral pH and draw their structures as they would occur in a salt bridge:



Asp – Arg | or any pair of: Asp, Glu — Lys, Arg, His

b) Consider two situations, one in which the two sidechains are near each other on the surface of the protein, and a second in which they are the same distance apart in the interior of the protein.

In which case would the energy of interaction be more favorable – explain briefly.

probably in interior because dielectric constant is lower, sidechain also likely to be less flexible.

c) If you could calculate the direct energy of interaction between the residues in the salt bridge accurately, do you think this would be a good estimate for how much the salt bridge would stabilize the folded state of the protein relative to the unfolded state? (explain succinctly)

stability is ΔG, energy is ΔH – to get ΔG would also need to calculate ΔS, which is much harder, solvent entropy effects, etc.

Problem 4.

Prof. Wemmer did a demonstration in class with a 'cold pack' – in which cooling occurred due to ammonium nitrate dissolving in water. He looked in a table and found that the ΔH value for this reaction is +20 kJ/mol (the chemical process absorbs heat).

a) If the packet contained 250 ml of water and one mole of ammonium nitrate, starting at 25°C, what will the temperature of the cold pack be when the dissolution is complete? (assume the ammonium nitrate does not affect properties of the water)

reaction absorbs 20 kJ of heat, must come from water

heat = $\Delta H = C_p \Delta T$ $\quad -20\text{kJ} = 4.2\,\text{J/g} \times 250\,\text{g} \times (T - 298)$

$\frac{-20{,}000}{4.2 \times 250} + 298 = 279\,\text{K}$ (6°C)

b) What quantitative statement can be made about the entropy change for this reaction?

spontaneous, we know $\Delta G < 0$ so $\Delta H - T\Delta S < 0$

$\Delta H < T\Delta S$ $\quad \frac{\Delta H}{T} < \Delta S$ $\quad$ so $\frac{20\,000}{298} < \Delta S$

(for reaction to start spontaneously at 298K)

Problem 5.

Consider a container with an ideal gas, and four different procedures that can be done. In all cases the gas begins at 25°C and two atm of pressure.

(A) expand the gas adiabatically against a constant pressure of 1 atm.

(B) expand the gas isothermally and reversibly to a final pressure of 1 atm.

(C) expand the gas adiabatically through a frit (so no work is done) to a final pressure of 1 atm.

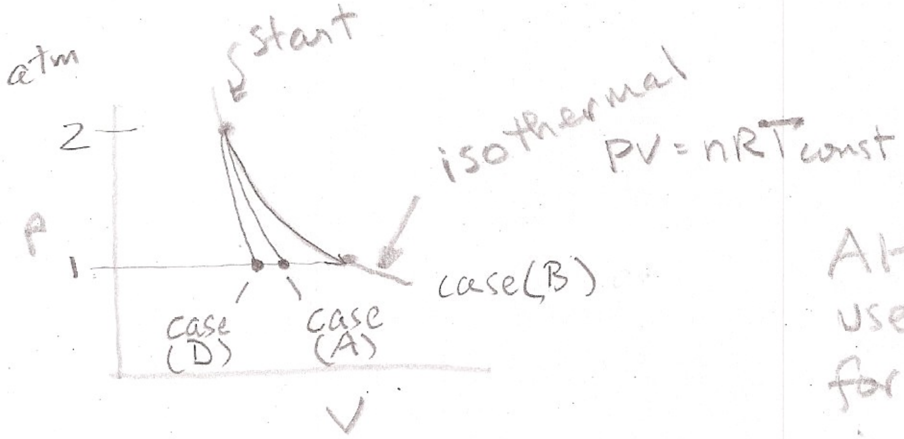
(D) expand the gas adiabatically and reversibly to a final pressure of 1 atm.

(note: circle all correct answers)

a) Which process(es) will leave the gas at the lowest temperature (circle) A B C (D)

b) Which process(es) will leave the gas at the highest temperature (circle) A (B) (C) D

c) Which two processes will have the same entropy change: B and C



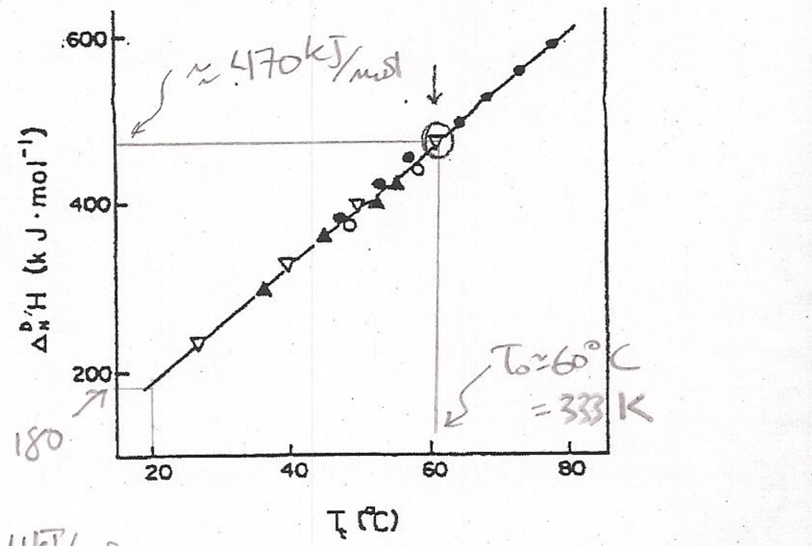
Although B and C use different paths, for each $\Delta U = \Delta H = \Delta T = 0$ since they reach the same state ΔS must be same

In (A) and (D) temperature drops because energy is taken out as work

reversible work takes out max work as expansion occurs, temp must drop faster than case (A)

Problem 6

Data from scanning calorimetry experiments are shown for the protein lysozyme, measured under a variety of different conditions to alter the melting temperature (horizontal axis) and the enthalpy of melting (vertical axis).



at T_m $\Delta S(T_m) = \frac{\Delta H(T_m)}{T_m}$

$= \frac{470{,}000}{333} = 1.4\,kJ/mol/K$

a) Consider the circled data point. Under those conditions that gave rise to that datapoint write out the equation for the protein stability as a function of temperature leaving temperature as the only variable (i.e. put in the numerical values for all constants for this protein):

$\Delta G(T) = \Delta H(T_0) - T\Delta S(T_0) + \Delta C_p(T - T_0 - T\ln T/T_0)$

$\Delta H(T_m) - \Delta H(T) = \Delta C_p \Delta T$ $\quad \frac{470\,kJ/mol - 180\,kJ/mol}{40K} = \Delta C_p$

$7.25\,kJ/mol/K = \Delta C_p$

so

$\Delta G(T) = 470\,kJ/mol - T(1.4\,kJ/mol/K) + 7.25\,\frac{kJ/mol}{K}\left(T - 333K - T\ln\frac{T}{333K}\right)$

b) Native lysozyme as used in these experiments has disulfide bonds between cystine residues in the polypeptide. If a reducing agent was added that reduced these to cysteine (Cβ-S-S-Cβ going to 2 x Cβ-SH) what will be the effect on the stability of the protein? Explain qualitatively what change you would expect in the protein stability equation above.

disulfides stabilize proteins by reducing the multiplicity (entropy) of the unfolded state – this effect should show up primarily in the $\Delta S(T_0)$ term