

Homework #7 Problems (#36-40)

In this problem set (and in the remainder of Chemistry 163B), you may use the differential expressions for the state functions U, H, A, and G as 'given' starting points.

36. E&R P6.20

Calculate ΔG for the isothermal expansion of 2.25 mol of an ideal gas at 325 K from an initial pressure of 12.0 bar to a final pressure of 2.5 bar.

also calculate ΔA for the same expansion.

37. E&R P6.5

38. E&R P6.26

39. Consider the equilibrium between two complementary DNA oligomer strands and the doubled-stranded duplex in the 'two-state' approximation.



- Write K_{eq} for the above equilibrium in terms of the concentrations $[S]$, $[S']$, and $[D]$.
- One measure of the stability of DNA and RNA oligomers is melting temperature, T_m , defined as the temperature at which 50% of the oligomer and its complement are in a doubled-stranded (duplex) configuration and 50% in a single stranded. Thus at T_m , there are equal amounts of oligomer strands in D and in $S + S'$: $2[D] = [S] + [S']$. If the single strands are mixed in equal initial concentrations with $C_T = [S]_0 + [S']_0 = 2[S]_0$, write an expression for the equilibrium constant at T_m , in terms of only C_T .
- Write an expression for T_m in terms of ΔH° and ΔS° for duplex formation and C_T .

(problem 39 continued on next page)

- d. It is found that ΔH° and ΔS° for this process can be well estimated by considering the interactions between nearest-neighbor base-pairs on S with their complement on S' [see "A unified view of polymer, dumbbell, and oligonucleotide DNA nearest-neighbor thermodynamics", *Proc. Natl. Acad. Sci. USA* Vol. 95, pp. 1460–1465, 1998].

Base pairs (NN)	ΔH° kJ mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹
AA/TT	-33.05	-92.88
AT/TA	-30.12	-85.35
TA/AT	-30.12	-89.11
CA/GT	-35.56	-94.97
GT/CA	-35.14	-93.72
GA/CT	-34.31	-92.88
CG/GC	-44.35	-113.81
GC/CG	-41.00	-102.09
GG/CC	-33.47	-83.26
G-C init	0.41	-11.72
A-T init	9.62	17.15

Using the table above estimate, ΔH° , ΔS° , and T_m for the two hexamer duplexes (for T_m , use $C_T = 10^{-3}$ M):

- i. 5'CGTTGA3'
3'GCAACT5'

With NN (nearest neighbor) interactions:

$$NN = (G-C)_{\text{initiation}} + \text{CG/GC} + \text{GT/CA} + \text{AA/TT} + \text{CA/GT} + \text{GA/CT} + (A-T)_{\text{initiation}}$$

- ii. *(optional)
5'AATTAA3'
3'TTAATT5'

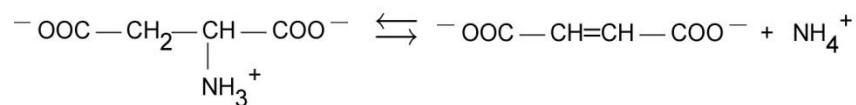
With NN (nearest neighbor) interactions:

$$NN = 2(A-T)_{\text{initiation}} + 3 \text{ AA/TT} + \text{AT/TA} + \text{TA/AT}$$

An automated program for calculating general oligonucleotide interactions can be accessed at: <http://www.idtdna.com/analyzer/Applications/OligoAnalyzer/> [needs cookies!] The ANALYZE function on this site is setup to run oligomers that bind to very dilute DNA sequences. To use this site is for part d. i and ii, you would enter the appropriate sequence, set Target Type=DNA, set Oligo Conc =250 μ M and set Na+ conc =1000 mM, then click ANALYZE to get MELT TEMP. Although this site purports to use the same PNAS parameters as above, you will get slightly different T_m 's.

[Literature reference: [SantaLucia, J. PNAS, 95, 1460-1465 \(1998\)](#)]

40. The deamination of aspartic acid:



is a reversible reaction catalyzed by the enzyme aspartase. For D,L-aspartic acid the equilibrium constant as function of temperature can be expressed by the equation:

$$\log K_{D,L} = 8.188 - \frac{a}{T} - bT \quad \text{where } a=2315.5 \text{ K and } b=0.01025 \text{ K}^{-1}$$

- What is ΔG° at 25° C? (in kJ mol⁻¹)
- Derive an equation for ΔH° as a function of T. (in kJ mol⁻¹)
- What is ΔH° at 25° C? (in kJ mol⁻¹)
- What is ΔS° at 25° C? (in J K⁻¹ mol⁻¹)
- * (optional) How are ΔH and ΔC_p related? Use this relationship to obtain ΔC_p° at 25° C for the deamination of aspartic acid.

[Literature reference: [J. L. Bada and S.L. Miller, *Biochemistry* 7, 3403, 1968](#)]