Homework #6
Problems (#36-#40)
Section Questions: Q6.4,Q6.5,Q6.12,Q6.13,Q6.16

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_{4th} P6.5
    a.
    b. also calculate ΔA for the same expansion.

37. E&R_{4th} P6.42

38. E&R_{4th} P6.9
    a. Show that $\left[\frac{\partial(A/T)}{\partial(1/T)}\right]_V = U$
    b. Write an expression analogous to Equations (6.32 and 6.33) that would allow you to relate Δ*A* at two temperatures.

    Equations (6.32-6.33) are:

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \int_{T_1}^{T_2} \Delta H \, d\left(\frac{1}{T}\right) \qquad (6.32)$$

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H(T_1)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (6.33)$$

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

$$\text{S} + \text{S}' \rightleftarrows \text{D (S-S}'\text{ duplex)}$$

    a. Write K_{eq} for the above equilibrium in terms of the concentrations [S], [S'], and [D].

    b. 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.

    c. 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:

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

ii. *(optional)
5'AATTAA3'
3'TTAATT5'
With NN (nearest neighbor) interactions:

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

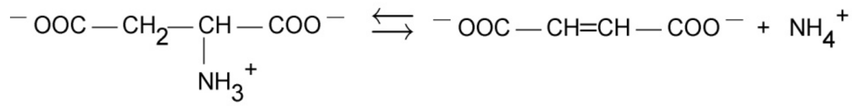
An automated program for calculating general oligonucleotide interactions can be accessed at: https://www.idtdna.com/calc/analyzer/

[account: **Chemistry163_UCSC** *password:* **Entropy163B***: and may need 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 =250μM 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:

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

a. What is $\Delta G°$ at 25° C? (in kJ mol^{-1})
b. Derive an equation for $\Delta H°$ as a function of T. (in kJ mol^{-1})
c. What is $\Delta H°$ at 25° C? (in kJ mol^{-1})
d. What is $\Delta S°$ at 25° C? (in J K^{-1} mol^{-1})
e. * (optional) How are ΔH and ΔC_p related? Use this relationship to obtain $\Delta C_p°$ at 25° C for the deamination of aspartic acid.

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