1. Match the items between these two columns about the thermodynamics parameters (Enthalpy, H; Gibbs free energy, G; Work, W; Entropy, S; Heat, q; Product, P; Reactant, R) (20 points)

(1) $q=\Delta H=0$	(A) $K_{eq} = 1$.
(2) $\Delta G>0$	(B) An ideal gas expands adiabatically into a vacuum.
(3) $\Delta G° = -RT \ln K_{eq}$	(C) An ideal gas expands isothermally against external pressure of 1 atm.
(4) $\Delta H=\Delta E=0$	(D) Used to determine standard Gibbs free energy.
(5) $\Delta G<0$	(E) An ideal gas expands adiabatically against external pressure of 1 atm.
(6) $\Delta G = \Delta H - T\Delta S$	(F) System at equilibrium.
(7) $q = w = \Delta H = \Delta E = 0$	(G) Reaction spontaneous as written.
(8) $\Delta G = \Delta G° + RT \ln([P]/[R])$	(H) Used to calculate amount of free energy released when reaction proceeds to equilibrium.
(9) $\Delta G = 0$	(I) Definition of change in Gibbs free energy.
(10) $\Delta G° = 0$	(J) Reaction unfavorable.

2. Use nearest-neibhbor values (Table 1) for the thermodynamics of double strand formation to calculate $\Delta G°$ (kcal/mol), $\Delta H°$ (kcal/mol) and $\Delta S°$ (cal/K·mol) for 5'-ATAGCA-3' & 5'-TGCTAT-3'. (10 points)

Table 1 $\Delta H°$ (kcal/mol) and $\Delta S°$ (cal/K·mol) for nearest neighbor calculation. All values refer to forming duplex at 1M NaCl, 25°C, and pH = 7.0. (Allawi & SantaLucia Biochemistry 1997). The separate strands are in antiparallel orientation (e.g., AC/TG means 5'-AC-3' paired with 3'-TG-5').

5'-3'/3'-5'	$\Delta H°$(kcal/mol)	$\Delta S°$(cal/K·mol)
AA/TT	-7.9	-22.2
AG/TC	-7.8	-21.0
AT/TA	-7.2	-20.4
AC/TG	-8.4	-22.4
GA/CT	-8.2	-22.2
GG/CC	-8.0	-19.9
GC/CG	-9.8	-24.4
TA/AT	-7.2	-21.3
TG/AC	-8.5	-22.7
CG/GC	-10.6	-27.2
Initiation	+0.2	-5.2

3. Write down the four steps in the Carnot cycle of an idealized heat engine with an ideal gas as its working substance and the change of ΔU (internal energy), ΔS (entropy), and ΔH (enthalpy) associated with each step, assuming the engine is working between the temperature T_1 and T_2. (20 points)

	Step 1	Step 2	Step 3	Step 4
Process				
ΔU				
ΔS				
ΔH				

4. There is evidence that a critical concentration of a trigger protein is needed for cell division. This unstable protein is continually being synthesized and degraded. The rate of protein synthesis controls how long it takes for the trigger protein to build up to the concentration necessary to start DNA synthesis and eventually to cause cell division. Let's choose a simple mechanism to consider quantitatively. The trigger protein *U* is being synthesized by a zero-order mechanism with a rate constant k_0. It is being degraded by a first-order mechanism with rate constant k_1.

(a) Write a differential equation consistent with the mechanism. (2 points)

(b) The solution to the correct differential equation is $[U]=\frac{k_0}{k_1}(1-e^{-k_1 t})$, if $[U]$ is equal to zero at zero time. Show that your equation in part (a) is consistent with this. (2 points)

(c) If *U* is being synthesized at a constant rate with $k_0 = 1.00\ nMs^{-1}$ and its half-life for degradation is 0.500 h, calculate the maximum concentration that *U* will reach. How long will it take to reach this concentration? (4 points)

(d) If a concentration of *U* of 1.00 μM is needed to trigger DNA synthesis and cell replication, how long will it take to reach this concentration? (4 points)

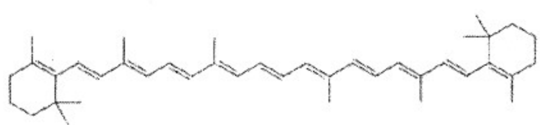
(e) If the rate of synthesis is cut in half ($k_0 = 0.500\ nMs^{-1}$), how long will it take for *U* to reach a concentration of 1.00 μM? (4 points)

(f) What is the smallest rate of *U* synthesis k_0 that will allow cell replication? Assume k_1 remains constant. (4 points)

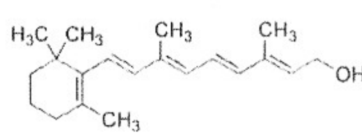
5. Assuming that a catalyst is not itself affected by temperature, do you expect the rate of the catalyzed or uncatalyzed reaction to be more sensitive to temperature changes? Explain. (5 points)

6. A simple noncompetitive inhibitor of acetylcholinesterase binds to the enzyme to affect V_{max} only; it does not affect K_M. For an inhibition constant of $K_I = 2.9 \times 10^{-4}$ M, what concentration of inhibitor is needed to give a 90% inhibition of the enzyme? (5 points)

7. The compound β-carotene is the precursor of retinol (vitamin A), which plays an important role in vision, bone growth, reproduction, cell division and cell differentiation. The β-carotene and retinol are both compounds with conjugated π systems and their structures are shown below. Can you predict which compound has UV/Visible absorption in the longer wavelength region due to the conjugated π systems? Explain why. (Hint: consider "particle in a box") (10 points)



β-carotene



retinol

8. According to the chemiosmotic theory, an electrochemical proton gradient is used to synthesize ATP in mitochondria. The enzyme that does this is located on the inside of the mitochondrial membranes. The oxidation of carbohydrates and fats is used to pump protons outside the mitochondrial membrane until the steady-state membrane potential is -140 mV and the pH gradient is ΔpH=1.5. Inside the mitochondria, pH = 7.0, [ATP]= 1 mM, $[P_i]$ = 2.5 mM, [ADP] = 1 mM, and T = 298 K. ($ATP + H_2O \rightarrow ADP + P_i \quad \Delta G^{0'} = -31.0\ kJ$)

(a) How much chemical potential is required to synthesize ATP inside the mitochondria? (4 points)

(b) How much free energy is made available by moving 1 mol of protons from the outside to the inside? Is this enough to drive ATP synthesis? (4 points)

(c) How many protons must be translocated per ATP synthesized? (2 points)