NAME:

1. When a protein is in its folded, native state it has one most stable conformation. When proteins are denatured, they become random coils having many possible conformations.

a. (5 pts) What sign do you expect ΔS to have for the process native fold → random coil?

$\Delta S > 0$

b. (5 pts) What can be said about the sign (and magnitude) of ΔH if proteins are considered stable structures?

$\Delta G = \Delta H - T\Delta S$ $\quad \Delta G > 0$ otherwise denaturization will be spontaneous

$\Delta H > 0$

$|\Delta H| > |T\Delta S|$

c. (5 pts) Would you expect that proteins would be more likely to denature with increasing or decreasing temperature? (explain your answer quantitatively)

As T increases the entropy term will dominate and ΔG will become negative, the process of denaturization will be spontaneous

2. One reaction in the glycolosis pathway is the isomerization of Glucose-6-phosphate (G6P) to Fructose-6-phosphate (F6P): G6P←→F6P $\Delta G° = +1.7$kJ/mol

a. (10 pts) What is the equilibrium constant for this reaction at 298K?

$\Delta G^\circ = -RT\ln K \Rightarrow K = e^{-\Delta G^\circ/RT}$

$K = e^{-1.7\times10^3 \text{ J mol}^{-1} / 8.31 \text{ J mol}^{-1}\text{K}^{-1} \cdot 298\text{K}} = 0.5035$

b. (10 pts) At equilibrium, what percent will be fructose-6-phosphate and what percent will be glucose-6-phosphate?

$G6P \rightleftharpoons F6P$

$[G6P] + [F6P] = 1$

$[F6P] = 1 - [G6P]$

$K = \frac{[F6P]}{[G6P]} = \frac{1-[G6P]}{[G6P]} = 0.5035$

$[G6P] = 66.5\%$

$[F6P] = 33.5\%$

NAME:

3. On his sixteenth birthday, Clark Kent was barely able to crush a small piece of structural steel requiring 30,000 psi of pressure (giving the maximum pressure of his grip). In his chemistry class, he learned that one could change graphite to diamond provided that enough pressure is applied. (Problem author: anonymous TA)

	H^0	S^0	G^0	Density
Graphite	0	5.74 J/(K mol)	0	2.25 g/cm^3
Diamond	1.90 kJ/mol	2.38 J/(K mol)	2.90 kJ/mol	3.51 g/cm^3

Atomic weight of Carbon = 12 g/mol

$\Delta G(P) = \Delta G(1\text{ atm}) + \Delta V(P - 1\text{atm})$

a. (10 pts) What pressure is necessary to turn graphite to diamond at 25 °C?

$$\Delta G(P) = 0 = \Delta G^0 - \Delta V(P - 1\text{atm}) \Rightarrow P = \frac{-\Delta G^\circ}{\Delta V} + 1\text{atm}$$

$$P = \frac{-2{,}900\ \text{J}}{12\left(\frac{1}{3.51} - \frac{1}{2.25}\right)\text{cm}^3 \ \frac{8.314\ \text{J}}{82.05\ \text{atm}\cdot\text{cm}^3}} + 1 = 14{,}700\ \text{atm}$$

b. (7.5 pts) Was Clark able to make Lana some home-made diamond earrings?

$$\frac{30{,}000\ \text{psi}}{14.7\ \text{psi/atm}} = 2040\ \text{atm} \Rightarrow \text{no such luck}$$

c. (7.5 pts) Since Clark can withstand high temperatures as well, would it be beneficial for him to go to the Smallville steel mill where the temperature exceeds 1000 °C? Briefly explain why or why not using thermodynamic principles.

No, since the entropy change is (−), an increase in the temperature will just make the rxn more difficult

$$\Delta G = \underbrace{\Delta H - T\Delta S}_{\text{both terms (+)}}$$

both terms (+) T↑, ΔG↑ ⇒ less spontaneous

NAME:

4. Starting with dG = dE + d(PV) - d(TS),

a. (10 pts) show that dG = dw*[rev] + VdP - SdT for any reversible change. Point out where the reversibility is important.
(Hint: reversible path dw = -PdV + dw*[rev] ; P = the system pressure)

$$dG = dE + PdV + VdP - TdS - SdT \quad \text{(product rule)}$$

$$dG = dq_{rev} + dw_{rev} + PdV + VdP - TdS - SdT \quad \text{(Choose a reversible path, as question asks)}$$

$dw = -P_{ex}dV + dw^*$ $\xrightarrow{\text{reversible}}$ $dw_{rev} = -PdV + dw^*_{rev}$
(↑ non P-V work) (↑ system pressure ($= P_{ex}$ for rev))

$dS = \frac{dq_{rev}}{T}$; definition of Entropy from reversible process

...tions ... for ... e processes ... cancelations ... e.

$$dG_{rev} = \cancel{dq_{rev}} - \cancel{PdV} + dw^*_{rev} + \cancel{PdV} + VdP \text{ [scribbled out] (oops)} - T\left(\cancel{\frac{dq_{rev}}{T}}\right) - SdT$$

$$= dw^*_{rev} + VdP - SdT \quad \text{(QED)}$$

b. (7.5 pts) What is dG for any reversible process that occurs entirely at constant T?

$$dG_{rev} = dw^*_{rev} + VdP - S\cancel{dT} \quad (\rightarrow 0 \text{ at const } T)$$

$$dG_{rev,T} = dw^*_{rev} + VdP$$

c. (7.5 pts) What is dG for any reversible process that occurs entirely at constant T and P?

$$dG_{rev,T} = dw^*_{rev} + d\cancel{VP} \quad (\rightarrow 0 \text{ at const } P)$$

$$dG_{rev,T,P} = dw^*_{rev}$$

NAME:

5. A very efficient motor protein, resembling the F_0F_1 ATP synthase, is discovered and experiments indicate that it is able to convert 92% of the free energy of ATP hydrolysis into mechanical work.

$$ATP \rightarrow ADP + Pi \qquad \Delta G° = -30 \text{ kJ/mol}$$

a. (7.5) How much total mechanical work is performed by the protein for each mole of ATP hydrolyzed? (The experimental conditions were [ATP] = [Pi] = 10^{-3} M and [ADP] = 100 10^{-6} M, T = 298 K, you can assume these concentrations and T do not change during the experiment)

$$\Delta G = \Delta G^{o} + RT \ln Q$$

$$= -30 \text{ kJ/mol} + 8.314 \times 298 \times \left[\ln \frac{100 \times 10^{-6} \times \cancel{10^{-3}}}{\cancel{10^{-3}}}\right] \times 10^{-3}$$

$$= -52.82 \text{ kJ/mol}$$

Mechanical Work = 92% × 52.82 kJ

= 48.60 kJ

b. (7.5) A new graduate student tries to reproduce the above experiment and consistently finds that the measured mechanical work differs from the result in part (a) by –4.2 kJ/mol (e.g. 4.2 kJ/mol more work done). Later we discover he forgot to dilute a stock solution of ATP, thus using a different ATP concentration in his experiment. What was [ATP] in his experiment?

$$-\frac{(48.60 + 4.2)}{92\%} = -30 + 8.314 \times 298 \times 10^{-3} \ln \frac{100 \times 10^{-6} \times 10^{-3}}{[ATP]}$$

$$\Rightarrow [ATP] = 6.31 \times 10^{-3} \text{ M}$$