

Problem Set #3

Chem 471

Fall 1999

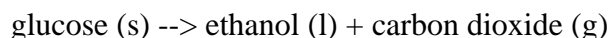
Due Wednesday, 9/29/99, in class.

Show your work. Problem sets will be spot graded. Work must be shown.

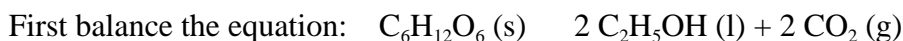
$$R = 0.08206 \text{ liter atm K}^{-1} \text{ mole}^{-1} = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$$

1. Some organisms such as yeast convert glucose to ethanol.

(a) Write a balanced equation for the process



and calculate H , q , w , and E for the reaction of 1 mole of glucose at 298K, 1 atm. Neglect the volumes of solids and liquids.



From back of book, $H = 2(-276.98) + 2(-393.509) - (-1274.4) = -66.58 \text{ kJ mol}^{-1}$

$q = q_p = H$ (this is constant P)

$$w = -P(V_2 - V_1) = -P \frac{nRT}{P} - 0 = -nRT = -(2)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298\text{K}) = -4955 \text{ J mol}^{-1}$$

$$E = q + w = [(-66.58) + (-4.955)] \text{ kJ mol}^{-1} = 71.54 \text{ kJ mol}^{-1}$$

(b) Suppose the same reaction is carried out by a thermophilic organism which lives at 80°C, 1 atm. Calculate H under these conditions. Ignore the heats of solution of the products and reactants. $C_p(\text{ethanol(l)}) = 111.5 \text{ J/moleK}$, $C_p(\text{glucose(s)}) = 210 \text{ J/moleK}$, $C_p(\text{carbon dioxide(g)}) = 37.1 \text{ J/moleK}$.

$$H_2 = H_1 + C_p(T_2 - T_1)$$

$$H_{f, \text{glucose}}^{T=353\text{K}} = (-1274.4 \text{ kJ mol}^{-1}) + (0.210 \text{ kJ mol}^{-1} \text{ K}^{-1})(353 - 298)\text{K} = -1262.9 \text{ kJ mol}^{-1}$$

$$H_{f, \text{ethanol}}^{T=353\text{K}} = (-276.98 \text{ kJ mol}^{-1}) + (0.1115 \text{ kJ mol}^{-1} \text{ K}^{-1})(353 - 298)\text{K} = -270.8 \text{ kJ mol}^{-1}$$

$$H_{f, \text{CO}_2}^{T=353\text{K}} = (-393.509 \text{ kJ mol}^{-1}) + (0.0371 \text{ kJ mol}^{-1} \text{ K}^{-1})(353 - 298)\text{K} = -391.5 \text{ kJ mol}^{-1}$$

Using these values, as before:

$$H = 2(-270.8) + 2(-391.5) - (-1262.9) = -61.7 \text{ kJ mol}^{-1}$$

(c) Suppose the same reaction is carried out at 1 atm in an insulated container so that no heat is lost to the surroundings. If the reaction occurs in 1 kg of water (again ignore heats of solution), what is the final state of the water -- temperature and phase? This time assume the total reaction solution has the same heat capacity as liquid water (4.18 kJ/kgK) and that the reaction itself occurs quickly -- it is complete at 298K, before any temperature changes can occur.

Using conditions from part (a), for 1 mole of glucose, 66.58 kJ is given off by the reaction.

In an isolated system, the energy cannot be dissipated to the surroundings and so goes to heating the aqueous solution. What temperature rise does 66.58 kJ contribute towards heating 1 kg of water?

$$66.58 \text{ kJ mol}^{-1} = (4.18 \text{ kJ kg}^{-1} \text{ K}^{-1})(1 \text{ kg}) (T_2 - 298) \text{ K}$$

$$T_2 = 298 \text{ K} + \frac{66.58 \text{ kJ mol}^{-1}}{(4.18 \text{ kJ kg}^{-1} \text{ K}^{-1})(1 \text{ kg})} = 298 \text{ K} + 15.9 \text{ K} = 314 \text{ K} = 40.9^\circ \text{ C}$$

(d) Which process a, b, or c does more work? Briefly explain why.

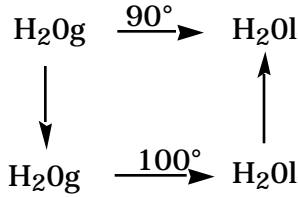
2. T,S,&W Ch 3 Pb 6

- This is a classic, if not a bit esoteric, problem - I didn't expect everyone to get this. The motor will not work (did you expect otherwise?). The stick intended to keep the ratchet from turning counter clockwise is also hit randomly by the gas molecules. Therefore there is no net rotation of the motor in any direction.
- This is harder. If the ratchet is at a lower temperature than the paddle, then the fluctuations in the stick (above) will be less. Work can be done by converting heat into work, and transferring heat from the high T paddle to the low T ratchet, in accord with the second law. It works, but of course, there is no free lunch, as hoped for in the first scenario.

3. T,S,&W Ch 3 Pb 15

100°, 1atm H₂O vapor H₂O liquid
reversibly, by removing heat

- S_{sys} decrease (liquid less disordered than gas)
- S_{universe} remain unchanged (S_{tot} = 0 for reversible process)
- G_{sys} zero (G = 0 for reversible process, @ constant T,P)
- Different values for real (non reversible) process for S_{universe}, S_{surr}
- S_{sys} decrease (gas liquid)
- S_{universe} remain unchanged (reversible)
- G_{sys} remain unchanged (reversible)
- S_{sys}(90) more negative than S_{sys}(100)



$$S(90) = C_p(g) = (100-90) + S(100) + C_p(l) (90-100)$$

$$= S(100) + \underbrace{(C_{p,l} - C_{p,g})}_{\ominus} (90-100)$$

$$S(90) < S(100)$$

4. T,S,&W Ch 3 Pb 17

- a) If more solvent is bound by the coil than by the helix, then both the enthalpy and the entropy can decrease (this is the reverse of what happens when proteins fold in water). This is a possible explanation. Since $S < 0$, increasing the temperature favors the reactant (coil), the unfolding is "less spontaneous."
- b) Yes, the reaction is spontaneous, because $G < 0$:

$$G = H - T S = -4.0 \text{kJmol}^{-1} - (312 \text{K})(-0.012 \text{kJK}^{-1} \text{mol}^{-1}) = -0.26 \text{kJmol}^{-1}$$

- c) We want the temperature at which the phase transition is poised at equilibrium ($G=0$)

$$G = 0 = H - T S$$

$$T = \frac{H}{S} = \frac{-4.0 \text{kJmol}^{-1}}{-0.012 \text{kJK}^{-1} \text{mol}^{-1}} = 330 \text{K} = 60^\circ \text{C}$$

- d) No. The 2nd law says that the entropy of an isolated system cannot decrease. Period.

5. T,S,&W Ch 3 Pb 24

- a) temperature: $(PV) = nRT$
- b) temperature
- c) increases
- d) equal to
- e) greater than
- f) P, T, G
- g) q will be smaller in magnitude (all of the variables except q and w are state variables!).

6. T,S,&W Ch 3 Pb 26

Isentropic - entropy does not change

Using equations 3.21 (pressure effect on entropy) and 3.15 (temperature effect on entropy)

$$S_2 - S_1 = S = 0 = -R \ln \frac{P_2}{P_1} + \bar{C}_p \ln \frac{T_2}{T_1}$$

$$\ln \frac{T_2}{T_1} = \frac{R}{\bar{C}_p} \ln \frac{P_2}{P_1}$$

$$\ln T_2 = \ln T_1 + \frac{R}{\bar{C}_p} \ln \frac{P_2}{P_1}$$

but the problem gave us that $\frac{\bar{C}_p}{R} = \frac{7}{2}$ and $T_1 = 298\text{K}$ at 760 mm pressure

$$\ln T_2 = \ln 298 + \frac{2}{7} \ln \frac{210}{760} = 5.33$$

$$T_2 = 206\text{K} = -67^\circ\text{C}$$

7. T,S,&W Ch 3 Pb 27

Placing the water in the freezer at -20°C results in a spontaneous transfer of (Gibbs) free energy:

$$\frac{G_{\text{freezing } -20^\circ\text{C}}}{253\text{K}} = \frac{G_{\text{freezing } 0^\circ\text{C}}}{273\text{K}} + \frac{1}{253\text{K}} - \frac{1}{273\text{K}} \quad H \quad (\text{equation 3.31 and nearby})$$

Remembering that $G_{\text{freezing } 0^\circ\text{C}, 1\text{atm}} = 0$, $H = 333.4\text{ kJ kg}^{-1}$, and multiplying by 273K :

$$G_{\text{freezing } -20^\circ\text{C}} = \frac{(253\text{K})(0)}{273\text{K}} + 253\text{K} \left(\frac{1}{253\text{K}} - \frac{1}{273\text{K}} \right) H = 253\text{K} \left(\frac{1}{253\text{K}} - \frac{1}{273\text{K}} \right) 333.4\text{ kJ kg}^{-1}$$

At the final equilibrium, G must be zero, so this is offset by a (Gibbs) free energy change given by:

$$G_{253}(P) = \int_{1\text{atm}}^{P_2} V dP = 0.0903 \frac{\text{mL}}{\text{g}} (P_2 - 1\text{atm}) \quad (\text{see equations 3.33 and 3.36})$$

"Is offset" means: $G_{\text{freezing } -20^\circ\text{C}} + G_{253}(P) = 0$, so:

$$-253\text{K} \left(\frac{1}{253\text{K}} - \frac{1}{273\text{K}} \right) 333.4\text{ kJ kg}^{-1} = 0.0903 \frac{\text{mL}}{\text{g}} (P_2 - 1\text{atm})$$

$$\left(-24.4\text{ kJ kg}^{-1} \right) \frac{\text{g}}{0.0903\text{mL}} = (P_2 - 1\text{atm})$$

$$P_2 = 1\text{ atm} + \left(-24.4\text{ kJ kg}^{-1} \right) \frac{\text{g}}{0.0903\text{mL}} \frac{0.08206\text{ L atm}}{8.314\text{ J}} \frac{\text{kg}}{1000\text{g}} \frac{1000\text{mL}}{\text{L}} \frac{1000\text{J}}{\text{kJ}}$$

$$P_2 = 1\text{ atm} + 2667\text{ atm} = 2668\text{ atm}$$