

Given: $g = 9.81 \text{ m/s}^2$
 $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
 $1 \text{ atm} = 1.0133 \times 10^5 \text{ Nm}^{-2} = 760 \text{ Torr}$
 $P = P_0 \exp\{-Mgh/RT\}$

$$P_2 = P_1 + \frac{\Delta_{trs}H_m}{\Delta_{trs}V_m} \ln\left(\frac{T_2}{T_1}\right) \quad , \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{trs}H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta S = -R \sum_{i=1}^N x_i \ln x_i \text{ where } N \text{ is the number of components}$$

$$\rho = mgh \quad , \quad P = \rho gh \quad , \quad dS \geq \frac{\delta q}{T} \quad , \quad dw = -PdV \quad , \quad dH = dU + PdV$$

Please answer all questions.

1. A. Diatomic oxygen makes up ~20% of the atmosphere. Assuming that the mole fraction of oxygen is 0.2 calculate the density of oxygen at sea level at 298 K. (5 points):

Solution: $\rho = PM/RT$
 $= (0.2 \times 1.01325 \times 10^5 \text{ Nm}^{-2})(0.032 \text{ kg/m}^3)/(8.31 \text{ J/mol-K})(298 \text{ K})$
 $= 0.262 \text{ kg/m}^3 = 0.262 \text{ g/L}$

$\rho(\text{g L}^{-1}) = \underline{0.262}$

- B. Calculate the root-mean-square velocity of diatomic oxygen gas at 400 K (5 points).

Solution: $\text{sqrt}\langle u^2 \rangle = \text{sqrt}(3RT/M) = \text{sqrt}(3(8.31 \text{ J/mol-K})(400 \text{ K})/0.032 \text{ kg/mol})$
 $= 558 \text{ m/s}$

$\text{sqrt}\langle u^2 \rangle = \underline{558 \text{ m/s}}$

- C. Calculate the molar heat capacity at constant pressure of diatomic oxygen gas at 400 K (5 points).

Solution: $C_p = 7/2R = (3.5)(8.31 \text{ J/mol-K})$
 $= 29.0 \text{ J/mol-K}$

$C_p = \underline{29.0 \text{ J/mol-K}}$

2. Estimate the molar configurational (statistical) entropy of a single-strand DNA consisting of 25 nucleotides assuming that each nucleotide can exist in the 3 different conformations. (5 points)

Solution: $S = R \ln W$ where $W = M^N$ (M is number of conformers per monomer and N is the number of monomers). Thus $S = NR \ln M = 25(8.31 \text{ J/mol-K})\ln 3 = 228.2 \text{ J/mol-K}$

$S = \underline{\underline{228.2 \text{ J/mol-K}}}$

3. A. Determine the molar entropy of mixing for 2 gases with equal mole fraction that are mixed together.
 B. Determine the molar entropy of mixing for 3 gases with equal mole fraction that are mixed together.
 C. Which is larger and why. (10 points)

Solution:

$$\Delta S = -R(x_1 \ln x_1 + x_2 \ln x_2) = -R(0.5 \ln(0.5) + 0.5 \ln(0.5))$$

$$= -R \ln(0.5) = (8.31 \text{ J/mol-K})(0.693) = 5.76 \text{ J/mol-K}$$

$$\Delta S = -R(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3) = -R(0.33 \ln(0.33) + 0.3 \ln(0.33) + 0.3 \ln(0.33))$$

$$= -R \ln(0.5) = (8.31 \text{ J/mol-K})(1.09) = 9.12 \text{ J/mol-K}$$

A. ΔS mixing (two gases) = $\underline{\underline{5.76 \text{ J/mol-K}}}$

B. ΔS mixing (three gases) = $\underline{\underline{9.12 \text{ J/mol-K}}}$

C. Your hypothesis: There more ways to distribute three different species than two species among the available energy levels. Explanations involving a greater disorder for three species than two were also accepted.

4. A. The thermodynamic efficiency of a steam turbine is 0.5 and the operating temperature is at 600 K. Please calculate the exhaust temperature (3 points).

Solution:

$$\eta = (T_{\text{hot}} - T_{\text{cold}})/T_{\text{hot}} \Rightarrow T_{\text{cold}} = T_{\text{hot}}(1 - \eta) = 600(0.5) = 300 \text{ K}$$

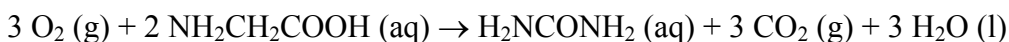
Exhaust temperature = $\underline{\underline{300 \text{ K}}}$.

- B. How much energy is lost as heat for every kJ of heat expelled into the environment by this engine (2 points)?

Solution: $\eta = |w|/q \rightarrow$ The work obtained is $|w| = \eta q = 0.5 \times 1 \text{ kJ} = 0.5 \text{ kJ}$ per kJ of heat generated. The heat lost is equal to $q_{\text{lost}} = q - |w| = 1 - 0.5 \text{ kJ} = 0.5 \text{ kJ}$.

Fraction of energy lost as heat = $\underline{\underline{0.5}}$.

5. The standard enthalpy for the metabolism of glycine is given by the equation:



The enthalpies of formation at 298 K are as follows:

aqueous glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) $\Delta_f H^\circ = -518 \text{ kJ/mol}$

aqueous urea ($\text{NH}_2\text{CH}_2\text{COOH}$) $\Delta_f H^\circ = -317 \text{ kJ/mol}$

carbon dioxide (CO_2) $\Delta_f H^\circ = -393.5 \text{ kJ/mol}$

water (H_2O) $\Delta_f H^\circ = -286 \text{ kJ/mol}$

A. Calculate $\Delta_{\text{rxn}} H^\circ$ at 298 K for the oxidation of glycine as written above (5 points).

$$3 \Delta_f H^\circ(\text{H}_2\text{O}) + 3 \Delta_f H^\circ(\text{CO}_2) + \Delta_f H^\circ(\text{H}_2\text{NCONH}_2) - 2 \Delta_f H^\circ(\text{NH}_2\text{CH}_2\text{COOH}) =$$

$$3(-286) + 3(-393.5) + (-317) - 2(-518) = -1319.5 \text{ kJ/mol}$$

Note: $\Delta_f H^\circ(\text{O}_2) = 0$ by definition.

$$\Delta_{\text{rxn}} H^\circ = \underline{\hspace{10em}} -1319.5 \text{ kJ/mol} \underline{\hspace{10em}}.$$

B. The third law entropies at 298 K and the heat capacities of the species are given in the table below. Assuming that the entropy and enthalpy are dependent on temperature calculate the Gibb's free energy at 310 K (15 points).

Substance	C_p (J/mol-K)	S° (J/mol-K)
$\text{NH}_2\text{CH}_2\text{COOH} (\text{aq})$	95	109
$\text{H}_2\text{NCONH}_2 (\text{aq})$	93	104
$\text{H}_2\text{O} (\text{l})$	75	70
$\text{CO}_2 (\text{g})$	37	214
$\text{O}_2 (\text{g})$	29	205

Solution:

$$\Delta S^\circ(298 \text{ K}) = 3S^\circ(\text{H}_2\text{O}) + 3S^\circ(\text{CO}_2) + S^\circ(\text{H}_2\text{NCONH}_2) - 2S^\circ(\text{NH}_2\text{CH}_2\text{COOH}) - 3S^\circ(\text{O}_2) =$$

$$3(70) + 3(214) + (104) - 2(109) - 3(205) = 123 \text{ J/mol-K}$$

$$\Delta C_p = 3C_p(\text{H}_2\text{O}) + 3C_p(\text{CO}_2) + C_p(\text{H}_2\text{NCONH}_2) - 2C_p(\text{NH}_2\text{CH}_2\text{COOH}) - 3C_p(\text{O}_2) =$$

$$3(75) + 3(37) + (93) - 2(95) - 3(29) = 152 \text{ J/mol-K}$$

$$\Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \Delta C_p \ln(T_2/T_1)$$

$$\Delta S^\circ(310 \text{ K}) = \Delta S^\circ(298 \text{ K}) + \Delta C_p \ln(310 \text{ K}/298 \text{ K}) = 123 + 152 \ln(310/298) = 129.0 \text{ J/mol-K}$$

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \Delta C_p(T_2 - T_1)$$

$$\Delta H^\circ(310 \text{ K}) = \Delta H^\circ(298 \text{ K}) + \Delta C_p(310 \text{ K} - 298 \text{ K}) = -1319.5 + 152(310 - 298) = -1317.7 \text{ kJ/mol}$$

$$\Delta G^\circ(310 \text{ K}) = \Delta H^\circ(310 \text{ K}) - T\Delta S^\circ(310 \text{ K}) = -1,317,700 - 310(129.0) = -1,357.3 \text{ kJ/mol}$$

$$\Delta_{\text{rxn}} G^\circ(310 \text{ K}) = \underline{\hspace{10em}} -1357.3 \text{ kJ/mol} \underline{\hspace{10em}}.$$

6. The binding constant of a drug at 300 K is $5.5 \times 10^7 \text{ M}^{-1}$ and at 310 K it is $1.2 \times 10^7 \text{ M}^{-1}$. Calculate the standard enthalpy and entropy change for the binding process (10 points).

Solution: Use the van't Hoff equation.

$$\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H^\circ = \frac{R \ln \left(\frac{K_2}{K_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{RT_1 T_2 \ln \left(\frac{K_2}{K_1} \right)}{(T_2 - T_1)}$$

Plugging in numbers we obtain:

$$\Delta H^\circ = \frac{(8.31 \text{ J/mol-K})(300 \text{ K})(310 \text{ K}) \ln \left(\frac{1.2 \times 10^7}{5.5 \times 10^7} \right)}{10 \text{ K}} = -117.6 \text{ kJ/mol}$$

At 300 K, $\Delta G^\circ = -RT \ln K = -(8.31 \text{ J/mol-K})(300 \text{ K}) \ln(5.5 \times 10^7) = -44.4 \text{ kJ/mol}$

$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = (-117600 - (-44400)) \text{ J/mol} / 300 \text{ K} = -244 \text{ J/mol-K}$.

$$\Delta_{\text{binding}} H^\circ = \underline{\underline{-117.6 \text{ kJ/mol}}}$$

$$\Delta_{\text{binding}} S^\circ = \underline{\underline{-244 \text{ J/mol-K}}}$$

7. Calculate the entropy change when 360 grams of boiling water are poured into a stainless steel bowl weighing 220 grams at 25 °C. Assume that the molar mass of the metal in the bowl is 55 grams/mole. The heat capacity of water is 75 J/mole-K and that of bowl is 25 J/mole-K. (10 points)

Solution: First we must calculate the equilibrium temperature.

$$\begin{aligned} T_{\text{eq}} &= \frac{n_1 C_{p1} T_1 + n_2 C_{p2} T_2}{n_1 C_{p1} + n_2 C_{p2}} \\ &= \frac{(20 \text{ mol})(75 \text{ J/mol-K})373 \text{ K} + (4 \text{ mol})(25 \text{ J/mol-K})298 \text{ K}}{(20 \text{ mol})(75 \text{ J/mol-K}) + (4 \text{ mol})(25 \text{ J/mol-K})} \\ &= 368.3 \text{ K} \end{aligned}$$

$$T_{\text{equilibrium}} = \underline{\underline{368.3 \text{ K}}}$$

Now we calculate the entropy change of the water and bowl separately.

The process is spontaneous. If you get a negative entropy for a heat transfer problem, you know that you have made a mistake somewhere. Heat transfer from a hotter to a colder body is always

$$\begin{aligned}\Delta S_{\text{water}} &= n_1 C_{p1} \left(\frac{T_{\text{eq}}}{T_1} \right) = (20 \text{ mol})(75 \text{ J/mol-K}) \ln \left(\frac{368.3}{373} \right) \\ &= -19 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{bowl}} &= n_2 C_{p2} \left(\frac{T_{\text{eq}}}{T_2} \right) = (4 \text{ mol})(25 \text{ J/mol-K}) \ln \left(\frac{368.3}{298} \right) \\ &= +21.2 \text{ J/K}\end{aligned}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{water}} + \Delta S_{\text{bowl}} = +2.2 \text{ J/K}$$

spontaneous.

$$\Delta S = \underline{\hspace{2cm} 2.2 \text{ J/K} \hspace{2cm}}.$$

8. Suppose that you are working for a company that wants to make diamond and they determine that they need a chemical potential (i.e. a free energy) of -80 kJ/mol for the reaction. Using the pressure dependence of the free energy determine the pressure required to yield this free energy. You are given the following data. The reaction is:



The standard free energy change of the reaction is $\Delta_r G^\circ = +2.9 \text{ kJ/mol}$.

The density of graphite is 2.26 g/cm^3 and the density of diamond is 3.51 g/cm^3 . (10 points)

Solution: The difference here is that we must use the full relationship including ΔG (since ΔG is not zero here!). We do the same thing we did in class. We solve for the pressure.

$$\begin{aligned}\Delta G &= \Delta G^\circ + \Delta V_m (P - 1) \\ P &= 1 + \frac{\Delta G - \Delta G^\circ}{\Delta V_m} = 1 + \frac{\Delta G - \Delta G^\circ}{\frac{M}{\rho_d} - \frac{M}{\rho_{gr}}} \\ &= 1 + \frac{-80000 \text{ J/mol} - 2900 \text{ J/mol}}{0.012 \text{ kg/mol} \left(\frac{1}{3510} - \frac{1}{2260} \right)} \\ &= 4.4 \times 10^{10} \text{ Pa} = 440 \text{ kilobars}\end{aligned}$$

$$\text{Pressure} = \underline{\hspace{2cm} 440 \text{ kilobars} \hspace{2cm}}.$$