

Homework #4

- 4.17 The absolute molar entropies of O_2 and N_2 are $205 \text{ J K}^{-1} \text{ mol}^{-1}$ and $192 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, at 25°C . What is the entropy of a mixture made up of 2.4 moles of O_2 and 9.2 moles of N_2 at the same temperature and pressure?

The entropy of the mixture, S_f , is related to the entropy of mixing, $\Delta_{\text{mix}}S$, and the initial entropy of the system, S_i . Before these quantities can be calculated, the mole fractions of O_2 and N_2 need to be determined.

$$x_{O_2} = \frac{2.4 \text{ mol}}{2.4 \text{ mol} + 9.2 \text{ mol}} = 0.207$$
$$x_{N_2} = 1 - 0.207 = 0.793$$

The entropy of mixing is

$$\begin{aligned}\Delta_{\text{mix}}S &= -R (n_{O_2} \ln x_{O_2} + n_{N_2} \ln x_{N_2}) \\ &= - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) [(2.4 \text{ mol}) \ln 0.207 + (9.2 \text{ mol}) \ln 0.793] \\ &= 49.2 \text{ J K}^{-1}\end{aligned}$$

The initial entropy of system is the sum of the entropies of O_2 and N_2 :

$$\begin{aligned}S_i &= n_{O_2} \bar{S}_{O_2} + n_{N_2} \bar{S}_{N_2} = (2.4 \text{ mol}) (205 \text{ J K}^{-1} \text{ mol}^{-1}) + (9.2 \text{ mol}) (192 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 2.26 \times 10^3 \text{ J K}^{-1}\end{aligned}$$

Since $\Delta_{\text{mix}}S = S_f - S_i$,

$$S_f = \Delta_{\text{mix}}S + S_i = 49.2 \text{ J K}^{-1} + 2.26 \times 10^3 \text{ J K}^{-1} = 2.3 \times 10^3 \text{ J K}^{-1}$$

- 4.21 A quantity of 0.35 mole of an ideal gas initially at 15.6°C is expanded from 1.2 L to 7.4 L. Calculate the values of w , q , ΔU , and ΔS if the process is carried out (a) isothermally and reversibly, and (b) isothermally and irreversibly against an external pressure of 1.0 atm.

(a) $\Delta U = 0$ for an isothermal process. Thus, $q = -w$.

$$\begin{aligned}w &= -nRT \ln \frac{V_2}{V_1} \\ &= - (0.35 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (288.8 \text{ K}) \ln \frac{7.4 \text{ L}}{1.2 \text{ L}} \\ &= -1.53 \times 10^3 \text{ J} \\ q &= 1.53 \times 10^3 \text{ J} \\ \Delta S &= \frac{q_{\text{rev}}}{T} = \frac{1.53 \times 10^3 \text{ J}}{288.8 \text{ K}} = 5.3 \text{ J K}^{-1}\end{aligned}$$

The final answers for q and w should be rounded to two significant figures, $q = 1.5 \times 10^3 \text{ J}$ and $w = -1.5 \times 10^3 \text{ J}$.

(b) $\Delta U = 0$ for an isothermal process. Thus, $q = -w$.

$$w = -P_{\text{ex}}\Delta V = -(1.0 \text{ atm})(7.4 \text{ L} - 1.2 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -6.28 \times 10^2 \text{ J}$$

$$q = 6.28 \times 10^2 \text{ J}$$

$$\Delta S = 5.3 \text{ J K}^{-1} \text{ [as calculated in part (a).]}$$

Recall that S is a state function, but ΔS has to be calculated using a reversible path. Again, the final answers for q and w should be rounded to two significant figures, $q = 6.3 \times 10^2 \text{ J}$ and $w = -6.3 \times 10^2 \text{ J}$.

4.25 The $\Delta_f \bar{H}^\circ$ values can be negative, zero, or positive, but the \bar{S}° values can be only zero or positive. Explain.

Since $S = k_B \ln W$ and W cannot be less than 1, S cannot be negative. On the other hand, the enthalpy change associated with the formation of one mole of a substance from its elements in their standard states may be negative, positive, or zero. That is, the formation reaction can be exothermic, endothermic, or thermoneutral.

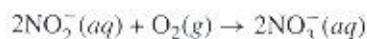
4.31 As an approximation, we can assume that proteins exist either in the native (or physiologically functioning) state or the denatured state. The standard molar enthalpy and entropy of the denaturation of a certain protein are 512 kJ mol^{-1} and $1.60 \text{ kJ K}^{-1} \text{ mol}^{-1}$, respectively. Comment on the signs and magnitudes of these quantities, and calculate the temperature at which the denaturation becomes spontaneous.

The enthalpy change for the denaturation of the protein is positive. It is an endothermic process, requiring energy to break up the hydrogen bonds and van der Waals interactions present in the native form. Some energy is returned due to additional protein-solvent (H_2O) intermolecular interactions in the denatured state. Nevertheless, the overall process is endothermic. Typical hydrogen bond enthalpies are $10 - 15 \text{ kJ mol}^{-1}$, so the value of 512 kJ mol^{-1} for $\Delta \bar{H}^\circ$ indicates that approximately 40 more hydrogen bonds were broken than were formed. Since the denaturation process takes the specific, ordered native form to a random form, $\Delta \bar{S}^\circ$ is expected to be positive, although solvent effects may also make a contribution.

The denaturation is spontaneous when $\Delta G = \Delta H - T\Delta S < 0$, or $T > \frac{\Delta H}{\Delta S}$. Since the values given are standard values, they apply only to a solution that is both 1 M in native form and 1 M in denatured form. For such a solution, the native form will spontaneously denature to reach a position of equilibrium when

$$\begin{aligned} T &> \frac{\Delta H^\circ}{\Delta S^\circ} \\ &> \frac{512 \text{ kJ mol}^{-1}}{1.60 \text{ kJ mol}^{-1}} \\ &> 320 \text{ K} = 47^\circ \text{ C} \end{aligned}$$

4.32 Certain bacteria in the soil obtain the necessary energy for growth by oxidizing nitrite to nitrate:



Given that the standard Gibbs energies of formation of NO_2^- and NO_3^- are $-34.6 \text{ kJ mol}^{-1}$ and $-110.5 \text{ kJ mol}^{-1}$, respectively, calculate the amount of Gibbs energy released when 1 mole of NO_2^- is oxidized to 1 mole of NO_3^- .

According to the chemical equation $2\text{NO}_2^-(aq) + \text{O}_2(g) \rightarrow 2\text{NO}_3^-(aq)$,

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f G^\circ [\text{NO}_3^-(aq)] - 2\Delta_f G^\circ [\text{NO}_2^-(aq)] - \Delta_f G^\circ [\text{O}_2(g)] \\ &= 2(-110.5 \text{ kJ mol}^{-1}) - 2(-34.6 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1} \\ &= -151.8 \text{ kJ mol}^{-1}\end{aligned}$$

When 1 mole of NO_2^- is oxidized to 1 mole of NO_3^- ,

$$\Delta_r G^\circ = \frac{-151.8 \text{ kJ mol}^{-1}}{2} = -75.9 \text{ kJ mol}^{-1}$$

4.35 A student placed 1 g of each of three compounds A, B, and C in a container and found that no change had occurred after one week. Offer possible explanations for the lack of reaction. Assume that A, B, and C are totally miscible liquids.

There are three possibilities, depending on the sign of $\Delta_r G$ for the expected changes.

- (1) No reactions are possible, $\Delta_r G > 0$.
 - (2) Reactions are possible thermodynamically, $\Delta_r G < 0$, but the rates are extremely slow.
 - (3) The three components are already at equilibrium, $\Delta_r G = 0$.
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- 4.37 Crystallization of sodium acetate from a supersaturated solution occurs spontaneously. What can you deduce about the signs of ΔS and ΔH ?

Since this is a spontaneous process, ΔG is negative. The solid phase of a substance is more ordered than the aqueous phase. Thus, ΔS is negative. Since $\Delta H = \Delta G + T\Delta S$, it must be negative. That is, this process is exothermic.

- 4.39 A certain reaction is spontaneous at 72°C . If the enthalpy change for the reaction is 19 kJ , what is the *minimum* value of $\Delta_r S$ (in joules per kelvin) for the reaction?

$$\Delta_r \bar{G} = \Delta_r H - T \Delta_r S < 0$$

$$19\text{ kJ} - (345\text{ K}) \Delta_r S < 0$$

$$\Delta_r S > \frac{19 \times 10^3\text{ kJ}}{345\text{ K}} = 55\text{ J K}^{-1}$$

Therefore, the minimum $\Delta_r S$ must be 55 J K^{-1} . At this value of $\Delta_r S$, the reaction is at equilibrium. At greater values of $\Delta_r S$, the reaction is spontaneous.

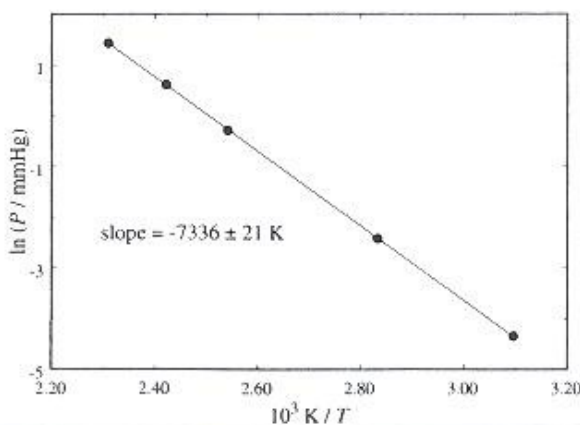
- 4.41 The vapor pressure of mercury at various temperatures has been determined as follows:

T/K	P/mmHg
323	0.0127
353	0.0888
393.5	0.7457
413	1.845
433	4.189

Calculate the value of $\Delta_{\text{vap}} \bar{H}$ for mercury.

A plot of $\ln P$ vs $1/T$ has a slope of $-\Delta_{\text{vap}} \bar{H}/R$, from which $-\Delta_{\text{vap}} \bar{H}$ is obtained.

$10^3\text{ K}/T$	$\ln P$
3.10	-4.3362
2.83	-2.4214
2.54	-0.29343
2.42	0.61248
2.31	1.4325



The slope of the best fit straight line to the data is -7300 K , where the value has been rounded to reflect the regression estimate of uncertainty in the slope. Thus,

$$\begin{aligned}-\frac{\Delta_{\text{vap}}\overline{H}}{R} &= -7300 \text{ K} \\ \Delta_{\text{vap}}\overline{H} &= -(-7300 \text{ K}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 6.07 \times 10^4 \text{ J mol}^{-1} \\ &= 61 \text{ kJ mol}^{-1}\end{aligned}$$