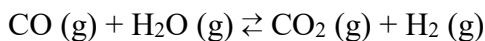


Chapter 15: Spontaneity

1. The water gas shift reaction is an important process in the gasification of coal or biomass to produce transportation fuels:



What is the relationship among the chemical potentials for the reaction at equilibrium?

Answer: At equilibrium: $\mu_{\text{CO}} + \mu_{\text{H}_2\text{O}} = \mu_{\text{CO}_2} + \mu_{\text{H}_2}$

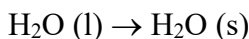
2. Some authors use “=” instead of “ \rightleftharpoons ” for chemical equations at equilibrium. For example:



Why is the use of the equals sign a good idea?

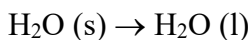
Answer: The equals sign is appropriate because the chemical potentials of the reactants and products are equal at equilibrium: $\mu_{\text{ATP}^{4-}} + \mu_{\text{H}_2\text{O}} = \mu_{\text{ADP}^{3-}} + \mu_{\text{HPO}_4^{2-}} + \mu_{\text{H}^+}$

3. Calculate $\Delta_{\text{fus}}H^\circ$, $\Delta_{\text{fus}}S^\circ$, and $\Delta_{\text{fus}}G^\circ$ for freezing one mole of supercooled water at -10.0°C and 1.00 bar pressure:



At 273.15 K, $\Delta_{\text{fus}}H^\circ = 6.008 \text{ kJ mol}^{-1}$. Assume the heat capacities are constant over the temperature range with $C_{p,m}(\text{s}) = 37.66 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_{p,m}(\text{l}) = 75.29 \text{ J K}^{-1} \text{ mol}^{-1}$.

Answer: Lets first work with the phase transition in the normal direction from low entropy phase to high entropy phase:



Then at the end we will reverse the direction to give the required results. We can use $\Delta_{\text{fus}}S^\circ = \Delta_{\text{fus}}H^\circ/T_m^*$, but only at the normal melting point, which is at 0°C :

$$\Delta_{\text{fus}}S^\circ = \Delta_{\text{fus}}H^\circ/T_m^* = 6.008 \times 10^3 \text{ J mol}^{-1} / 273.15 \text{ K} = 22.00 \text{ J K}^{-1} \text{ mol}^{-1}$$

The change in heat capacity for the phase transition is:

$$\Delta_{\text{fus}}C_p = C_p(\text{l}) - C_p(\text{s}) = (75.29 - 37.66) \text{ J K}^{-1} \text{ mol}^{-1} = 37.63 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{At } -10^\circ\text{C: } \Delta_{\text{fus}}S_{T_2}^\circ &= \Delta_{\text{fus}}S_{T_1}^\circ + \Delta_{\text{fus}}C_p \ln(T_2/T_1) \\ &= 22.00 \text{ J K}^{-1} \text{ mol}^{-1} + (37.63 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(263.15/273.15) = 20.59 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{fus}}H_{T_2}^\circ &= \Delta_{\text{fus}}H_{T_1}^\circ + \Delta_{\text{fus}}C_p (T_2 - T_1) \\ &= 6.008 \text{ kJ mol}^{-1} + 37.63 \text{ J K}^{-1} \text{ mol}^{-1} (-10.0 \text{ K})(1 \text{ kJ}/1000\text{J}) = 5.632 \text{ kJ mol}^{-1} \end{aligned}$$

The Gibbs energy change at -10°C is then:

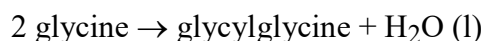
$$\begin{aligned}\Delta_{\text{fus}}G_{T_2}^\circ &= \Delta_{\text{fus}}H_{T_2}^\circ - T_2 \Delta_{\text{fus}}S_{T_2}^\circ && \text{for } \text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)} \\ &= 5.632 \text{ kJ mol}^{-1} - 263.15 \text{ K} (20.59 \text{ J K}^{-1} \text{ mol}^{-1})(1\text{kJ}/1000 \text{ J}) \\ &= 5.632 \text{ kJ mol}^{-1} - 5.419 \text{ kJ mol}^{-1} = 0.213 \text{ kJ mol}^{-1}\end{aligned}$$

The direction for the transition in the original problem is the reverse of this process giving:

$$\Delta_{\text{tr}}G_{T_2}^\circ = -0.213 \text{ kJ mol}^{-1} \quad \text{for } \text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (s)}$$

It is not surprising that the result is small, since at 273.15 K , $\Delta_{\text{tr}}G^\circ = 0$. However at -10°C , the result is negative as it should be, since the freezing of water is spontaneous at $T < 0^\circ\text{C}$.

4. Determine the energy necessary to form a peptide bond by determining $\Delta_r G^\circ$ for the following reaction at 298.2 K :



Use the data table below.

Substance	$\Delta_f H_m^\circ$ (kJ mol ⁻¹)	S_m° (J K ⁻¹ mol ⁻¹)
glycine	-528.5	103.5
glycylglycine	-747.7	190.0
H ₂ O (l)	-285.830	69.92

Answer: The trick is to remember that the thermodynamic potentials are extensive, so we need to take into account the stoichiometric coefficients.

	2 glycine → glycylglycine + H ₂ O (l)			units
$\Delta_f H_m^\circ$	-537.2	-745.3	-285.8	kJ mol ⁻¹
S_m°	103.5	190.0	69.9	J K ⁻¹ mol ⁻¹
$\Delta_f H_m^\circ$	-528.5	-747.7	-285.83	kJ mol ⁻¹
S_m°	103.5	190.0	69.92	J K ⁻¹ mol ⁻¹

Then the reaction changes are given by:

$$\begin{aligned}\Delta_r H^\circ &= \sum_{i=1}^{n_s} \nu_i \Delta_f H^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\ &= [1(-285.83 \text{ kJ mol}^{-1}) + 1(-747.7 \text{ kJ mol}^{-1})] - [2(-528.5 \text{ kJ mol}^{-1})] \\ &= 23.47 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r S^\circ &= \sum_{i=1}^{n_s} \nu_i S^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\ &= [1(69.92 \text{ J K}^{-1} \text{ mol}^{-1}) + 1(190.0 \text{ J K}^{-1} \text{ mol}^{-1})] - [2(103.5 \text{ J K}^{-1} \text{ mol}^{-1})] \\ &= 52.92 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

and from the definition of the Gibbs energy change for the reaction:

$$\begin{aligned}\Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ = 23.47 \text{ kJ} - 298.15 \text{ K}(52.92 \text{ J K}^{-1})(1 \text{ kJ}/1000\text{J}) \\ &= 7.7 \text{ kJ mol}^{-1}\end{aligned}$$

This final result is per mole of peptide bonds formed: $\Delta_r G_m^\circ = 7.7 \text{ kJ mol}^{-1}$ under standard state conditions. In living cells, the energy to drive this reaction is provided by the hydrolysis of ATP.

5. The enzyme pyruvate decarboxylase catalyzes the following reaction:



Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$, and $\Delta_r G^\circ$ for this reaction at 298.2K given the following data. Is this process enthalpy or entropy driven?

substance	$\Delta_f H_m^\circ$ (kJ mol ⁻¹)	$\Delta_f G_m^\circ$ (kJ mol ⁻¹)
acetaldehyde	-166.19	-128.86
CO ₂ (g)	-393.509	-394.359
pyruvic acid	-584.5	-463.4

$$\begin{aligned}\text{Answer: } \Delta_r H^\circ &= \sum_{i=1}^{n_s} v_i \Delta_f H^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\ &= [1(-166.19 \text{ kJ mol}^{-1}) + 1(-393.509 \text{ kJ mol}^{-1})] - [1(-584.5 \text{ kJ mol}^{-1})] \\ &= 24.80 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\circ &= \sum_{i=1}^{n_s} v_i \Delta_f G^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\ &= [1(-128.86 \text{ kJ mol}^{-1}) + 1(-394.359 \text{ kJ mol}^{-1})] - [1(-463.4 \text{ kJ mol}^{-1})] \\ &= -59.82 \text{ kJ mol}^{-1}\end{aligned}$$

Using the definition of the Gibbs energy allows the calculation of the entropy change for the reaction:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad \text{or} \quad \Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{[24.80 \text{ kJ} - (-59.82 \text{ kJ})](1000 \text{ J}/1 \text{ kJ})}{298.2 \text{ K}}$$

giving $\Delta_r S^\circ = 284. \text{ J K}^{-1}$. This process is entropy driven. The fact that CO₂ is a gas, which is a high entropy state, and also chemically quite stable helps make this reaction favorable under standard state conditions.

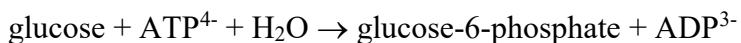
6. Before glucose can be used as an energy source in your body, it must first be phosphorylated:



the energy for this process is supplied by the hydrolysis of ATP:

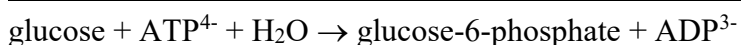


at pH 7. The overall reaction is then:



Calculate the entropy change for the overall reaction at 298.2 K from the given values of $\Delta_r G^\circ$ and $\Delta_r H^\circ$. Is the phosphorylation of glucose enthalpy or entropy driven?

Answer: According to Hess's law when chemical reactions are added, the enthalpies and Gibbs energies also add. In other words, enthalpy and Gibbs energy are state functions:



$$\text{Overall: } \Delta_r G^\circ = 16.7 \text{ kJ mol}^{-1} + (-31.0 \text{ kJ mol}^{-1}) = -14.3 \text{ kJ mol}^{-1}$$

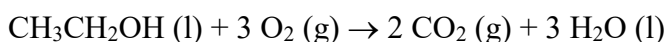
$$\Delta_r H^\circ = 35.1 \text{ kJ mol}^{-1} + (-24.3 \text{ kJ mol}^{-1}) = 10.8 \text{ kJ mol}^{-1}$$

Using the definition of the Gibbs energy allows the calculation of the entropy change for the reaction:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad \text{or} \quad \Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{10.8 \text{ kJ mol}^{-1} - (-14.3 \text{ kJ mol}^{-1})}{298.2 \text{ K}}$$

giving $\Delta_r S^\circ = 84.2 \text{ J K}^{-1} \text{ mol}^{-1}$ at pH 7. This process is entropy driven.

7. Ethanol is used as an additive in gasoline to increase the octane rating and to help decrease air pollution. Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$, and $\Delta_r G^\circ$ for the combustion of ethanol at 298.2 K using standard data tabulations:



Answer: The relevant data from the data tables in the appendix are given in below.

Substance at 298.15 K	$\Delta_f G^\circ$ (kJ mol ⁻¹)	$\Delta_f H^\circ$ (J K ⁻¹ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
CH ₃ CH ₂ OH (l)	-174.2	-277.0	161.0
O ₂ (g)	0	0	205.029
CO ₂ (g)	-394.359	-393.509	213.74
H ₂ O (l)	-237.178	-285.830	69.92

$$\begin{aligned} \Delta_r G^\circ &= \sum_{i=1}^{n_s} \nu_i \Delta_f G^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\ &= [2(-394.359 \text{ kJ mol}^{-1}) + 3(-237.178 \text{ kJ mol}^{-1})] - [1(-174.2 \text{ kJ mol}^{-1}) + 3(0)] \\ &= -1326.05 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_r S^\circ = \sum_{i=1}^{n_s} \nu_i S^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}]$$

$$\begin{aligned}
 &= [2(213.74 \text{ J K}^{-1} \text{ mol}^{-1}) + 3(69.92 \text{ J K}^{-1} \text{ mol}^{-1})] - [1(161.0 \text{ J K}^{-1} \text{ mol}^{-1}) + 3(205.029)] \\
 &= -138.85 \text{ J K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta_r H^\circ &= \sum_{i=1}^{n_s} \nu_i \Delta_f H^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\
 &= [2(-393.509 \text{ kJ mol}^{-1}) + 3(-285.830 \text{ kJ mol}^{-1})] - [1(-277.0 \text{ kJ mol}^{-1}) + 3(0)] \\
 &= -1367.51 \text{ kJ mol}^{-1}
 \end{aligned}$$

As a check, we should also find $\Delta_r G^\circ$ using:

$$\begin{aligned}
 \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ \\
 &= -1367.51 \text{ kJ mol}^{-1} - 298.15 \text{ K}(-138.85 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\
 &= -1326.11 \text{ kJ mol}^{-1}
 \end{aligned}$$

which certainly agrees to within the experimental error.

8. Why can we choose the Gibbs energy of formation of an element, in its most stable state at 1 bar pressure, as equal to zero?

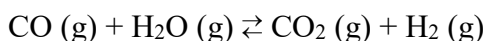
Answer: In practical circumstances, we always determine the difference in internal energy, enthalpy, entropy, Helmholtz energy, and Gibbs energy for a process: ΔU , ΔH , ΔS , ΔA , and ΔG . Therefore, the reference point is arbitrary. Figure 8.4.1 applies equally to Gibbs energy differences.

9. The enthalpy change for a reaction can be endothermic or exothermic. The entropy change for a chemical reaction can be positive or negative. Consider the temperature dependence of the spontaneity of a chemical reaction at constant pressure. Assume that the sign of the reaction enthalpy and entropy don't change with temperature. Under what cases, for the signs of the enthalpy and the entropy, is a reaction always spontaneous? Under what cases is a reaction never spontaneous?

Answer: Since $\Delta_r G = \Delta_r H - T \Delta_r S$ for a constant temperature process, the relative weighting of the enthalpy and entropy terms depends on temperature. Assuming that the sign of the reaction enthalpy and entropy don't change with temperature, if the enthalpy change is exothermic and the entropy change is positive, the reaction is spontaneous at all temperatures. If the enthalpy change is endothermic and the entropy change is negative, the reaction is non-spontaneous at all temperatures. If the enthalpy is exothermic and the entropy change is negative, or conversely if the enthalpy change is endothermic and the entropy change is positive, the sign of ΔG changes with temperature.

$\Delta_r H$	$\Delta_r S$	$\Delta_r G$
-	+	- always spontaneous
-	-	spontaneous at low T
+	+	spontaneous at high T
+	-	+ non-spontaneous

10. The water gas shift reaction is an important process in the gasification of coal or biomass to produce transportation fuels:



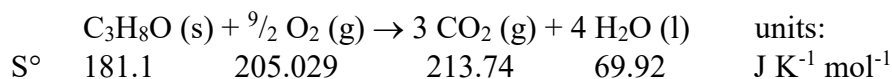
What is the relationship between the Gibbs and Helmholtz reaction energy changes at constant pressure? Why?

Answer: Since the change in the number of moles of gases is zero, $\Delta_r n_g = 0$, the Helmholtz and Gibbs energy changes for the reaction are the same: $\Delta_r G = \Delta_r A$. The reason is that no PV work is done since the volume is constant, for all practical purposes.

11. The internal energy of combustion of iso-propyl alcohol is $-2003.2 \text{ kJ mol}^{-1}$ at 298.2 K and 1.000 bar. The absolute entropy of iso-propyl alcohol is $180.58 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.2 K and 1.000 bar. Calculate the enthalpy, Helmholtz energy, and Gibbs energy of combustion of iso-propyl alcohol. Treat all gases as ideal.

Answer: The plan is to use the “thermodynamic cube,” Figure 15.4.1, and the balanced combustion reaction. In addition, from Eqs. 8.3.1° and 8.3.2°, $\Delta_r(PV) = \Delta_r n_{\text{gas}} RT$.

The balanced reaction is $\text{C}_3\text{H}_8\text{O (s)} + \frac{9}{2} \text{O}_2 \text{ (g)} \rightarrow 3 \text{CO}_2 \text{ (g)} + 4 \text{H}_2\text{O (l)}$, giving $\Delta_r n_{\text{gas}} = 3 - \frac{9}{2} = -\frac{3}{2}$. The change in entropy is given from standard tabulations as:



giving: $\Delta_r S = \Delta_c S = [\Sigma \text{products}] - [\Sigma \text{reactants}]$

$$\Delta_c S = [3(213.74) + 4(69.92)] - [1(181.1) + \frac{9}{2}(205.029)] \text{ J K}^{-1} \text{ mol}^{-1} = -182.83 \text{ J K}^{-1} \text{ mol}^{-1}$$

The entropy change is negative because the number of moles of gases decreases for the reaction. The definitions of the state functions and Figure 15.4.1 gives:

$$\begin{aligned} \Delta_c H &= \Delta_c U + \Delta_r n_{\text{gas}} RT \\ &= -2003.2 \text{ kJ mol}^{-1} + (-\frac{3}{2})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -2003.2 \text{ kJ mol}^{-1} - 3.718 \text{ kJ mol}^{-1} = -2006.9 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_c A &= \Delta_c U - T \Delta_c S \\ &= -2003.2 \text{ kJ mol}^{-1} - 298.15 \text{ K}(-182.83 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -1948.69 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned}\Delta_c G &= \Delta_c H - T\Delta_c S \\ &= -2006.9 \text{ kJ mol}^{-1} - 298.15 \text{ K}(-182.83 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -1952.39 \text{ kJ mol}^{-1}\end{aligned}$$

As a check, we can use:

$$\Delta_c G = \Delta_c A + \Delta_r n_{\text{gas}} RT = -1948.69 \text{ kJ mol}^{-1} - 3.718 \text{ kJ mol}^{-1} = -1952.41 \text{ kJ mol}^{-1}$$

The magnitude of the total maximum work available is less than $|\Delta_c U|$ because of the unfavorable change in entropy. However, more non-PV work is available than total work, $|\Delta_c G| > |\Delta_c A|$, because the surroundings do work on the system, since the number of moles of gas and the corresponding volume of the system decreases.

12. Calculate the change in Gibbs energy when one mole of an ideal gas expands isothermally from an initial volume of 1.00 L to a final volume of 10.0 L at 298.15 K.

Answer: For an isothermal expansion of an ideal gas, Eq. 15.4.6°:

$$\begin{aligned}\Delta G &= -nRT \ln(V_2/V_1) = -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(10.0/1.00) \\ &= -5.708 \times 10^3 \text{ J} = -5.71 \text{ kJ}\end{aligned}$$

13. Calculate the changes in Gibbs energy and Helmholtz energy when one mole of an ideal gas expands isothermally from an initial pressure of 2.00 bar to a final pressure of 1.00 bar at 298.15 K.

Answer: For an isothermal expansion, using Eq. 15.4.4°:

$$\begin{aligned}\Delta G &= nRT \ln(P_2/P_1) = (1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(1.00 \text{ bar}/2.00 \text{ bar}) \\ &= -1.718 \times 10^3 \text{ J} = -1.72 \text{ kJ}\end{aligned}$$

For the change in Helmholtz energy, we can use Eq. 15.4.2°, $\Delta A = -nRT \ln(V_2/V_1)$. From the ideal gas law:

$$V_1 = nRT/P_1 = 1.00 \text{ mol}(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/2.00 \text{ bar} = 12.39 \text{ L}$$

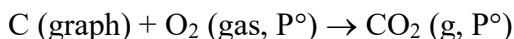
$$V_2 = nRT/P_2 = 1.00 \text{ mol}(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/1.00 \text{ bar} = 24.79 \text{ L}$$

$$\begin{aligned}\Delta A &= -nRT \ln(V_2/V_1) = -(1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(24.79/12.39) \\ &= -1.719 \times 10^3 \text{ J} = -1.72 \text{ kJ}\end{aligned}$$

Alternatively, for an isothermal process in an ideal gas, substituting $V_2/V_1 = P_1/P_2$ into Eq. 15.4.2° gives $\Delta A = -nRT \ln(V_2/V_1) = -nRT \ln(P_1/P_2) = nRT \ln(P_2/P_1) = \Delta G$. So $\Delta A = \Delta G$ for an isothermal process in an ideal gas, as shown in Chap. 15.4, but this time for the expressions written in terms of pressures.

14. General Chemistry texts often use a standard state pressure of 1 atm instead of 1 bar. Does the change in standard state make a significant difference in the tabulated values? Calculate the standard state Gibbs energy of formation for CO_2 at $P^\circ = 1 \text{ atm}$, given that the 1 bar standard state is $\Delta_f G^\circ(\text{CO}_2) = -394.36 \text{ kJ mol}^{-1}$ at 298.15 K.

Answer: The 1 bar standard state is just slightly less than the 1 atm standard state, 1 atm = 1.01325 bar. To a good approximation, we only need consider the gaseous reactants and products in a chemical reaction. The change in Gibbs energy for each reactant and product gas is given by Eq. 15.4.4°, assuming the gases are ideal. The formation reaction:



however, has an equal number of moles of reactant and product gases, so the change with pressure is zero, assuming ideal gas behavior. The 1 bar and 1 atm standard state reaction Gibbs energies are identical, for moderate changes in pressure.

15. General Chemistry texts often use a standard state pressure of 1 atm instead of 1 bar. Does the change in standard state make a significant difference in the tabulated values for Gibbs energies of formation? Calculate the standard state Gibbs energy of formation for SO_3 at $P^\circ = 1 \text{ atm}$ assuming ideal gas behavior, given that the 1 bar standard state is $\Delta_f G^\circ(\text{SO}_3, P^\circ = 1 \text{ bar}) = -371.06 \text{ kJ mol}^{-1}$ at 298.15 K.

Answer: The 1 bar standard state is just slightly less than the 1 atm standard state, 1 atm = 1.01325 bar. To a good approximation, we only need consider the gaseous reactants and products in a chemical reaction. The change in Gibbs energy for each reactant and product gas is given by Eq. 15.4.4°, assuming the gases are ideal. For reactant or product i :

$$G_i(P_i) - G_i(P^\circ) = n_i RT \ln P_i/P^\circ$$

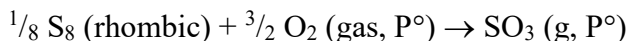
where P_i is the new pressure for reactant or product i and P° is the old standard state value. The n_i are given by the stoichiometric coefficients for a chemical reaction, $n_i = \nu_i$. The total change in Gibbs energy with the new pressures is then given by the difference of the products minus the reactants:

$$\Delta_r G = \Delta_r G^\circ + \sum \nu_i RT \ln P_i/P^\circ \quad (\nu_i \text{ for gases only})$$

If the P_i are identical for all the reactants and products, then the last equation reduces to:

$$\Delta_r G = \Delta_r G^\circ + \Delta_r n_g RT \ln P_i/P^\circ \quad (P_i \text{ equal for all species})$$

where $\Delta_r n_g = \sum \nu_i$ with the sum over all the gas phase species. The formation reaction:

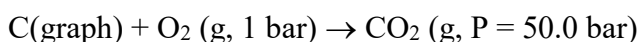


gives $\Delta_r n_g = -1/2$. The change in reaction Gibbs energy with pressure is then:

$$\begin{aligned} \Delta_r n_g RT \ln P_i/P^\circ &= \\ &= -\frac{1}{2} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln (1.01325 \text{ bar}/1.0000 \text{ bar}) = -16.32 \text{ J mol}^{-1} \\ \Delta_f G^\circ(\text{SO}_3, P^\circ = 1 \text{ atm}) &= -371.06 \text{ kJ mol}^{-1} - 0.01632 \text{ kJ mol}^{-1} = -371.08 \text{ kJ mol}^{-1} \end{aligned}$$

Even though this difference seems to be insignificant, the change in value translates into a ~1% difference in an equilibrium constant involving a reaction of one mole of SO_3 at 298 K (using $\Delta_r G^\circ = -RT \ln K_{\text{eq}}$).

16. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the Gibbs energy of formation for CO_2 at 50.0 bar and 298.15 K, relative to the constituent elements in their standard states:



Assume ideal gas behavior and $\Delta_f G^\circ(\text{CO}_2) = -394.36 \text{ kJ mol}^{-1}$ at 298.15 K.

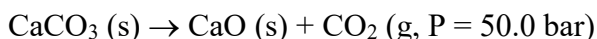
Answer: The change in Gibbs energy is given by Eq. 15.4.4°, assuming the CO_2 is ideal.

$$\begin{aligned} \Delta G_i &= n_i RT \ln P_2/P_1 = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J}) 298.15 \text{ K} \ln 50.0 \text{ bar}/1 \text{ bar} \\ &= 9.70 \text{ kJ mol}^{-1} \end{aligned}$$

Which gives the enthalpy of formation as:

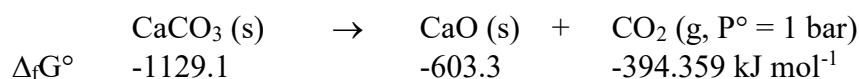
$$\begin{aligned} \Delta_f G &= \Delta_f G^\circ + 9.70 \text{ kJ mol}^{-1} \\ &= -394.36 \text{ kJ mol}^{-1} + 9.70 \text{ kJ mol}^{-1} = -384.66 \text{ kJ mol}^{-1} \end{aligned}$$

17. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the reaction Gibbs energy at 50.0 bar and 298.2 K for:



One crystalline form of CaCO_3 is the mineral calcite. Neglect the effect of the pressure on the solids and assume ideal gas behavior.

Answer: Under standard state conditions:



$$\begin{aligned} \Delta_r G^\circ &= \sum_{i=1}^{n_s} \nu_i \Delta_f G^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] \\ &= [(-394.359) + (-603.3)] - [-1129.1] \text{ kJ mol}^{-1} = 131.44 \text{ kJ mol}^{-1} \end{aligned}$$

The Gibbs energy of each gaseous reactant and product is then adjusted for the new pressure:

$$\Delta_r G = \Delta_r G^\circ + \sum \nu_i RT \ln P_i/P^\circ \quad (\nu_i \text{ for gases only})$$

as derived in the previous problems. The ν_i are the stoichiometric coefficients for each gaseous reactant and product, with ν_i negative for reactants. (See Chapter 20 for more information on non-standard state reaction Gibbs energies). For this reaction $\nu_{\text{CO}_2} = 1$ is the only gas:

$$\Delta_r G = \Delta_r G^\circ + RT \ln P_2/P_1^\circ$$

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln 50.0 \text{ bar}/1 \text{ bar} \\ &= 131.44 \text{ kJ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln 50.0 \\ &= 131.44 \text{ kJ mol}^{-1} + 9.70 \text{ kJ mol}^{-1} = 141.4 \text{ kJ mol}^{-1}\end{aligned}$$

18. Derive Eq. 15.4.8, $\Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2$, from $dG = V dP$ for an isothermal process, from an initial pressure P_o and a final pressure P .

Answer: The approximation $\Delta G = V_o (P - P_o)$ is at the “good” level, which assumes the volume is essentially unchanged for a small change in pressure. At the “better” level for moderate changes in pressure, we use Eq. 7.6.28, $V = V_o - V_o \kappa_T (P - P_o)$, with P_o the initial pressure and P the final pressure. The change in Gibbs energy with pressure for an isothermal process is given by the thermodynamic force, $(\partial G/\partial P)_T = V$ or $dG = V dP$. Integration using Eq. 7.6.28 gives:

$$\begin{aligned}\int_{G_o}^G dG &= \int_{P_o}^P V_o - V_o \kappa_T (P - P_o) dP = V_o \int_{P_o}^P dP - V_o \kappa_T \int_{P_o}^P (P - P_o) dP \\ \Delta G &= V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2 \Big|_{P_o}^P\end{aligned}$$

Applying the integral limits for the second term gives:

$$\begin{aligned}\Delta G &= V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2 + \frac{1}{2} V_o \kappa_T (P_o - P_o)^2 \\ \Delta G &= V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2\end{aligned}$$

19. Calculate the change in Gibbs energy for one mole of liquid benzene at 298.2 K for a change in pressure from 1.00 bar to 600.0 bar. The isothermal compressibility of benzene is $90.9 \times 10^{-6} \text{ bar}^{-1}$ and the density is 0.8765 g/cm^3 . Compare the results using Eqs. 15.4.7 and 15.4.8

Answer: The molar volume is:

$$V_o = 1 \text{ mol}(78.11 \text{ g mol}^{-1})/(1 \text{ m}^3/1 \times 10^6 \text{ cm}^3)/0.8765 \text{ g cm}^{-3} = 8.912 \times 10^{-5} \text{ m}^3$$

Using the more approximate formula gives:

$$\Delta G = V_o (P - P_o) = 8.912 \times 10^{-5} \text{ m}^3 (599.0 \text{ bar})(1 \times 10^5 \text{ Pa}/1 \text{ bar}) = 5338. \text{ J}$$

Converting the isothermal compressibility to Pa^{-1} is most convenient for this problem:

$$\kappa_T = 90.9 \times 10^{-6} \text{ bar}^{-1} (1 \text{ bar}/1 \times 10^5 \text{ Pa}) = 90.9 \times 10^{-11} \text{ Pa}^{-1}$$

Using the first-order correction for the volume change gives:

$$\begin{aligned}\Delta G &= V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2 \\ &= 5338. \text{ J} - \frac{1}{2} (8.912 \times 10^{-5} \text{ m}^3)(90.9 \times 10^{-11} \text{ Pa}^{-1})(599.0 \times 10^5 \text{ Pa})^2 \\ &= 5338. \text{ J} - 145.0 \text{ J} = 5193. \text{ J} = 5.193 \text{ kJ}\end{aligned}$$

The volume change correction term is chemically significant at this high pressure. Ultra-high pressure high performance liquids chromatographs, UHPLC, routinely operate at 600 bar using standard organic solvents for the mobile phase. Microwave assisted organic synthesis is routinely operated at 120 bar. The pressure at the bottom of the Mariana Trench is ~1,100 bar, so high pressures are accessible both in and outside the laboratory. However, for pressures near sea level ambient pressure, the more approximate formula, $\Delta G = V_o (P - P_o)$, is adequate for liquids and solids.

20. Calculate the Gibbs energy difference for one mole of water at the bottom of the Mariana Trench compared to 1 bar pressure, given $\kappa_T = 4.587 \times 10^{-10} \text{ Pa}^{-1}$ at 20°C. The maximum depth of the trench is 10911 m (35798 ft) and the pressure is 1,086. bar (15,750 psi). Use the density of pure water, 0.9982 g mL⁻¹ at 1 bar, for this problem, instead of the density of sea water.

Answer: The plan is to compare Eqs. Eq. 15.4.7 and 15.4.8. The molar volume of water at 1 bar is:

$$V_o = 1 \text{ mol}(18.015 \text{ g mol}^{-1})(1 \text{ m}^3/1 \times 10^6 \text{ cm}^3)/ 0.9982 \text{ g cm}^{-3} = 1.8048 \times 10^{-5} \text{ m}^3$$

Using the more approximate formula gives:

$$\Delta G = V_o (P - P_o) = 1.8048 \times 10^{-5} \text{ m}^3(1085.0 \text{ bar})(1 \times 10^5 \text{ Pa}/1 \text{ bar}) = 1958. \text{ J}$$

Using the first-order correction for the volume change gives:

$$\begin{aligned} \Delta G &= V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2 \\ &= 1958. \text{ J} - \frac{1}{2} (1.8048 \times 10^{-5} \text{ m}^3)(4.587 \times 10^{-10} \text{ Pa}^{-1})(1085.0 \times 10^5 \text{ Pa})^2 \\ &= 1958. \text{ J} - 97.5 \text{ J} = 1861. \text{ J} = 1.861 \text{ kJ} \end{aligned}$$

Note the final comments for the previous problem. The relatively small change in Gibbs energy with pressure is the reason that we don't normally need to correct for changes in pressure in thermochemical problems for liquids and solids.

21. Starting from $\Delta A = -nRT \ln V_2/V_1$ and the definition of G, in the form $G \equiv A + PV$, show that $\Delta G = nRT \ln P_2/P_1$, for an ideal gas in an isothermal process.

Answer: Using $G = A + PV$ and $PV = nRT$ for an ideal gas gives:

$$\Delta G = \Delta A + \Delta(PV) = \Delta A + nR\Delta T.$$

For an isothermal process $\Delta T = 0$ and then $\Delta G = \Delta A = -nRT \ln V_2/V_1$, using Eq. 15.4.2°. For an ideal gas $V_2/V_1 = P_1/P_2$, so then as we showed in Eqs. 15.4.5°-15.4.6°:

$$\Delta G = \Delta A = -nRT \ln V_2/V_1 = -nRT \ln P_1/P_2 = nRT \ln P_2/P_1$$

22. Reverse osmosis is the most cost effective method for seawater desalinization. However, reverse osmosis is energy intensive. In reverse osmosis, seawater is pressurized to 60-70 bar to

force water to flow through a semi-permeable membrane. The work in reverse osmosis can be estimated using $w = -P\Delta V$, where P is the constant high pressure of the process and ΔV is the volume of water pushed through the membrane. Calculate the change in Helmholtz energy for purifying 1.00 m^3 of water using reverse osmosis with an applied pressure of 65.0 bar. Give your results in joules and kWh ($1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$). Why is the change in Helmholtz energy salient for water desalination?

Answer: The plan is to note that the change in Helmholtz energy for a process is the total work for the process. Integrating Eq. 15.4.1, $dA = -P dV$, at constant pressure gives $\Delta A = -P \Delta V$, which is the work required for the process:

$$\Delta A = -P \Delta V = -65.0 \text{ bar}(1 \times 10^5 \text{ Pa}/1 \text{ bar})(1.00 \text{ m}^3) = -65.0 \times 10^5 \text{ J} = -6.5 \times 10^3 \text{ kJ}$$

The conversion from kWh to joules is $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$, Problem 2.12. The pressure is generated by electrical pumps requiring:

$$\Delta A = -65.0 \times 10^5 \text{ J}(1 \text{ kWh}/3.6 \times 10^6 \text{ J}) = 1.81 \text{ kWh m}^{-3}$$

If power is $\$ 0.10 (\text{kWh})^{-1}$, the cost is $\$ 0.18 \text{ m}^{-3}$, assuming 100% efficiency. The overall efficiency is more likely to be near 50%, giving a minimum cost of $\$ 0.36 \text{ m}^{-3}$ for processing alone. Daily indoor per capita water use in a US home is 69.3 gallons or $0.262 \text{ m}^3 \text{ day}^{-1} \text{ person}^{-1}$. World total fresh water consumption is over 2,000 billion $\text{m}^3 \text{ yr}^{-1}$. The Helmholtz energy change is the total work for the process, which is PV work for reverse osmosis. However, the result is a change in composition for dissolved salts, which is a chemical energy change, which is reflected by a change in Gibbs energy. Reverse osmosis converts mechanical work to chemical work.

23. How big of an effect does an electric field have on the electrochemical potential of an ion? Consider a simple electrochemical cell, $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$. Assume the electric potential is 0.500 V at the cathode. Calculate the electrochemical potential for one mole of Cu^{2+} ions, at standard state concentration, in the cathode (right-hand) compartment. In the absence of a field, $\Delta_f G_m^\circ$ for Cu^{2+} from standard tables is $65.49 \text{ kJ mol}^{-1}$.

Answer: The electrochemical potential is given by Eq. 15.3.9: $\bar{\mu}_i \equiv \mu_i + z_i F \phi_i$. The charge on a mole of Cu^{2+} ions is $z_i = 2 \text{ mol}$.

$$\begin{aligned} \bar{\mu}_{\text{Cu}^{2+}} &= \mu_{\text{Cu}^{2+}} + 2 \text{ mol } F (0.5 \text{ V}) \\ &= 65.49 \text{ kJ mol}^{-1} + 2 \text{ mol } (96485 \text{ C mol}^{-1})(0.500 \text{ V})(1 \text{ kJ}/1000 \text{ J}) \end{aligned}$$

Remembering that $1 \text{ J} = 1 \text{ C V}$:

$$= 65.49 \text{ kJ mol}^{-1} + 96.49 \text{ kJ mol}^{-1} = 161.98 \text{ kJ mol}^{-1}$$

The electric field component makes a significant contribution to the Gibbs energy of an ion in solution with an electric field. Another way of saying this is that 0.50 V is a significant voltage.

24. Two solutions containing K^+ ions are separated by a K^+ ion-selective membrane. Electrodes are placed in both solutions and the flow of K^+ ions is monitored as a function of applied potential, $\Delta\phi = \phi_{in} - \phi_{out}$. The K^+ ions cease migration across the membrane for an applied potential of -70.0 mV. Calculate the difference in chemical potential of the K^+ ions in the two solutions.

Answer: The plan is to note that when the ion flow is zero, the system is at equilibrium and $\Delta G = \bar{\mu}_{in} - \bar{\mu}_{out} = 0$.

Using Eq. 15.3.15 at equilibrium gives:

$$\Delta G = \bar{\mu}_{in} - \bar{\mu}_{out} = (\mu_{in} + z_+ F \phi_{in}) - (\mu_{out} + z_+ F \phi_{out}) = 0$$

Solving for the difference in chemical potential gives:

$$\mu_{in} - \mu_{out} = -z_+ F (\phi_{in} - \phi_{out}) = -z_+ F \Delta\phi$$

Hopefully, you remember this relationship from the treatment of electrochemistry in your General Chemistry course, where $\Delta\phi = E_{cell}$. For this specific problem, $z_+ = 1$ at -70.0 mV:

$$\mu_{in} - \mu_{out} = -1 (96485 \text{ C mol}^{-1})(-70.0 \times 10^{-3} \text{ V})(1 \text{ kJ}/1000 \text{ J}) = 6.75 \text{ kJ mol}^{-1}$$

Substantial differences in chemical potential are generated by simple concentration differences. This potential difference is a typical resting state potential for a nerve cell.

25. Coastal communities may be able to exploit the Na^+ gradient between seawater and fresh river water to generate electricity. Calculate the electric potential available from a seawater-fresh water cell with a Na^+ ion selectively-permeable membrane. Assume the difference in chemical potential, in the absence of electric fields, between seawater and fresh water is 10.5 kJ mol^{-1} (roughly a factor of 100 difference in concentration with an activity coefficient for 0.5 m NaCl of 0.680).

Answer: The plan is to note that the maximum potential difference is for the system at equilibrium, for which $\Delta G = \bar{\mu}_{in} - \bar{\mu}_{out} = 0$, and $z_+ = 1$ for NaCl.

From the previous problem we determined that at equilibrium:

$$\begin{aligned} \mu_{in} - \mu_{out} &= -z_+ F (\phi_{in} - \phi_{out}) = -z_+ F \Delta\phi \\ 10.5 \times 10^3 \text{ J mol}^{-1} &= -1(96485 \text{ C mol}^{-1}) \Delta\phi \qquad \text{giving } \Delta\phi = 0.109 \text{ V} \end{aligned}$$

Even though the voltage is small, the volume of the ocean is vast, which could potentially generate huge electrical currents. The limiting factors are the supply of fresh water and the large-scale availability of robust ion-selective membranes. The estimates for global production of energy from the seawater-fresh water interface are in the terawatts range.

26. The standard state Gibbs energy of formation of liquid water at 298.15 K is $-237.13 \text{ kJ mol}^{-1}$. Normally, we ignore any changes of $\Delta_f G^\circ$ with pressure for liquids and solids if the specific

reaction is run near 1 bar of pressure. How big of an error does this make? Calculate the change in Gibbs energy for one mole of liquid water for a pressure change from 1.00 bar to 50.0 bar.

Answer: Using Eq. 15.4.7 will be sufficiently accurate for this problem. For one mole, the initial volume is the pure molar volume of water:

$$\begin{aligned} V_o &= \mathcal{V}_{\text{H}_2\text{O}}/d_{\text{H}_2\text{O}} = 18.02 \text{ g mol}^{-1} / 0.99705 \text{ g mL} = 18.07 \text{ mL} \\ &= 18.07 \text{ mL} (1 \text{ m}^3/1 \times 10^6 \text{ mL}) = 1.807 \times 10^{-5} \text{ m}^3 \end{aligned}$$

From Eq. 15.4.7:

$$\Delta G = V_o \Delta P = 1.807 \times 10^{-5} \text{ m}^3 (50.0 \text{ bar} - 1.0 \text{ bar}) (1 \times 10^5 \text{ Pa}/1 \text{ bar}) = 88.54 \text{ J} = 0.0885 \text{ kJ}$$

Even such a large change in pressure gives a very small change in the Gibbs energy of the mole of water.

27. Calculate the change in Helmholtz energy and Gibbs energy for the vaporization of 1.00 mol of liquid water at 372.76 K and 1.00 bar. The enthalpy of vaporization at 372.76 K is 40.7 kJ mol⁻¹. Treat water vapor as an ideal gas. What does the difference between the Helmholtz and Gibbs energies tell you about the process? (The standard boiling point of water is 99.61 °C or 372.76 K.)

Answer: The phase transition occurs at the equilibrium phase transition temperature, so $\Delta_{\text{tr}}G = 0$. $\Delta_{\text{tr}}A$ is given by the work necessary to push back the atmosphere for the formation of one mole of water vapor, Eq. 15.4.18°:

$$\Delta_{\text{tr}}A = -n_{\text{gas}} RT_{\text{tr}} = -1.00 \text{ mol} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (373.15 \text{ K}) (1 \text{ kJ}/1000 \text{ J}) = -3.10 \text{ kJ}$$

The Gibbs energy change is the net work at constant temperature and pressure; Gibbs energy does not include PV work. The Helmholtz energy change is the total work available from the process at constant temperature. The vaporization process is at equilibrium, so no net work is available. However, the system expands as one mole of liquid is vaporized and the Helmholtz energy reflects the work done by the expansion. The sign of $\Delta_{\text{tr}}A$ is negative because the system does work against the surroundings, decreasing the energy of the system.

28. Calculate the change in Gibbs energy for the vaporization of 2.00 mol of liquid water at 372.76 K and 1.000 bar to give water vapor at 0.500 bar and the same temperature. Assume the vapor is ideal. (The standard boiling point of water is 99.61 °C or 372.76 K.)

Answer: We divide the process into two steps: step one, the vaporization of 2.00 mol of water at the standard boiling point and 1.000 bar pressure, and step two, the vapor pressure is lowered to 0.500 bar at constant temperature. For step one, under standard conditions, the transition is at equilibrium and $\Delta_{\text{tr}}G = 0$. For step two, the vapor is expanded isothermally to give:

$$\begin{aligned}\Delta G &= nRT \ln P_2/p_1 = 2.00 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(372.76 \text{ K}) \ln 0.500/1.000 \\ &= -4297. \text{ J} = -4.30 \text{ kJ}\end{aligned}$$

29. Show that for small changes in temperature the last two terms cancel in Eq. 15.4.15:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o} \approx -S_o (T - T_o)$$

To prove this relationship, expand the logarithmic term in a Taylor series and keep just the first non-zero term. (Note: the Taylor series expansion for $\ln(x_2/x_1) \approx x_2/x_1 - 1$, for $x_2/x_1 \approx 1$.)

Answer: First flip the numerator and denominator in the logarithmic term:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) + C_p T \ln \frac{T_o}{T}$$

The Taylor series expansion for $\ln(x_2/x_1) \approx x_2/x_1 - 1$, for $x_2/x_1 \approx 1$. Substitution gives:

$$\begin{aligned}\Delta G &\approx -S_o (T - T_o) + C_p (T - T_o) + C_p T (T_o/T - 1) \\ &\approx -S_o (T - T_o) + C_p (T - T_o) + C_p (T_o - T) \\ &\approx -S_o (T - T_o)\end{aligned}$$

So simply integrating $dG = -S dT$, with $S \approx S_o$ a constant over the temperature range isn't too bad for very narrow temperature ranges. However, in the next Chapter we will find a much better approximation that is easy to use and takes into account the change in entropy with temperature (Eq. 16.3.14, the Gibbs-Helmholtz equation).

30. Prove Eq. 15.4.15, that is $\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o}$.

Answer: We need to integrate $dG = -S dT$. The change in entropy for a constant pressure process, starting with initial entropy of S_o is:

$$S = S_o + C_p \ln \frac{T}{T_o}$$

Substitution into $dG = -S dT$ gives:

$$dG = -S dT = -(S_o + C_p \ln \frac{T}{T_o}) dT$$

Integration assuming a constant heat capacity gives:

$$\Delta G = -S_o \int_{T_o}^T dT - C_p \int_{T_o}^T \ln T dT + C_p \ln T_o \int_{T_o}^T dT$$

Integrating using $\int \ln x dx = x \ln x - x$:

$$\Delta G = -S_o (T - T_o) - C_p (T \ln T - T \Big|_{T_o}^T + C_p \ln T_o (T - T_o)$$

Applying the integral limits and multiplying out terms:

$$\Delta G = -S_o (T - T_o) - C_p (T \ln T - T) + C_p (T_o \ln T_o - T_o) + C_p T \ln T_o - C_p T_o \ln T_o$$

Cancelling terms:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p (T \ln T - T \ln T_o)$$

Combining the ln terms:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o}$$

31. Calculate the standard state Gibbs energy of formation for H₂S (g) at 500.0 K. Remember that the Gibbs energy of formation is for a chemical reaction and not just a pure substance. The relevant data are given in the table below.

Substance at 298.15 K	$\Delta_f G^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	C_p° (J K ⁻¹ mol ⁻¹)
H ₂ S (g)	-33.56	205.79	34.23
H ₂ (g)	0	130.684	28.824
S (s, rhombic)	0	31.80	22.64

Answer: The plan is to note that Eq. 15.4.15 is for a pure substance at standard state pressure with $\Delta G = G_T - G_o$:

$$G_T^\circ - G_o^\circ = -S_o^\circ (T - T_o) + C_p^\circ (T - T_o) - C_p^\circ T \ln \frac{T}{T_o}$$

For a chemical reaction from *General Pattern §8 Thermodynamic Relationships for Reactions* the last equation becomes:

$$\Delta_r G_T^\circ - \Delta_r G_o^\circ = -\Delta_r S_o^\circ (T - T_o) + \Delta_r C_p^\circ (T - T_o) - \Delta_r C_p^\circ T \ln \frac{T}{T_o}$$

where $\Delta_r S_o^\circ$ is the standard state reaction entropy at the reference temperature, T_o .

For the given reaction H₂ (g) + S (s, rhombic) → H₂S (g):

$$\Delta_r S_o^\circ = [1(205.79)] - [1(130.684) + 1(31.80)] \text{ J K}^{-1} \text{ mol}^{-1} = 43.306 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r C_p^\circ = [1(34.23)] - [1(28.824) + 1(22.64)] \text{ J K}^{-1} \text{ mol}^{-1} = -17.23 \text{ J K}^{-1} \text{ mol}^{-1}$$

Neglecting the terms for the temperature dependence of the reaction entropy gives:

$$\Delta_r G_T^\circ = \Delta_r G_o^\circ - \Delta_r S_o^\circ (T - T_o)$$

$$\begin{aligned} \Delta_r G_{500\text{K}}^\circ &= -33.56 \text{ kJ mol}^{-1} - 43.306 \text{ J K}^{-1} \text{ mol}^{-1} (500.0 \text{ K} - 298.2 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -33.56 \text{ kJ mol}^{-1} - 8.739 \text{ kJ mol}^{-1} = -42.299 \text{ kJ mol}^{-1} \end{aligned}$$

The more exact expression gives:

$$\begin{aligned} \Delta_r G_T^\circ &= \Delta_r G_o^\circ - \Delta_r S_o^\circ (T - T_o) + \Delta_r C_p^\circ (T - T_o) - \Delta_r C_p^\circ T \ln \frac{T}{T_o} \\ &= -42.30 \text{ kJ mol}^{-1} + (-17.23 \text{ J K}^{-1} \text{ mol}^{-1})(500.0 \text{ K} - 298.2 \text{ K})(1 \text{ kJ}/1000 \text{ J}) - \\ &\quad (-17.23 \text{ J K}^{-1} \text{ mol}^{-1})(500.0 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln \frac{500.0 \text{ K}}{298.2 \text{ K}} \\ &= -42.299 \text{ kJ mol}^{-1} - 3.477 \text{ kJ mol}^{-1} + 4.453 \text{ kJ mol}^{-1} = -41.32 \text{ kJ mol}^{-1} \end{aligned}$$

H₂S is an important component in exhaust from sewage treatment plants, in volcanic gases, and is also produced in large quantities by bacteria in the oceans. H₂S is also a byproduct of coal combustion, although most sulfur in coal is oxidized to SO₂. The H₂S and dimethylsulfide from aquatic bacteria is processed in clouds to form H₂SO₄ over the oceans. Oceanic H₂SO₄ reacts with NaCl particles to produce Na₂SO₄ aerosols that act as efficient cloud condensation nuclei. The extent of cloud cover is important in determining the extent of global climate change.

32. Calculate the standard state Gibbs energy of formation for SO₂ (g) at 500.0 K.

Answer: The plan is to note that Eq. 15.4.15 is for a pure substance. Remember that the Gibbs energy of formation is for a chemical reaction and not just a pure substance. The relevant data from the data tables in the appendix are given in the table below.

Substance at 298.15 K	$\Delta_f G^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	C_p° (J K ⁻¹ mol ⁻¹)
SO ₂ (g)	-300.194	248.223	39.87
O ₂ (g)	0	205.029	29.355
S (s, rhombic)	0	32.054	22.64

In the previous problem we showed that for a chemical reaction Eq. 15.4.15 becomes:

$$\Delta_r G_T^\circ - \Delta_r G^\circ = -\Delta_r S^\circ (T - T_0) + \Delta_r C_p^\circ (T - T_0) - \Delta_r C_p^\circ T \ln \frac{T}{T_0}$$

where $\Delta_r S^\circ$ is the standard state reaction entropy at the reference temperature, T_0 . For the given reaction O₂ (g) + S (s, rhombic) → SO₂ (g):

$$\begin{aligned}\Delta_r S^\circ &= [1(248.223)] - [1(205.029) + 1(32.054)] \text{ J K}^{-1} \text{ mol}^{-1} = 11.140 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_r C_p^\circ &= [1(39.87)] - [1(29.355) + 1(22.64)] \text{ J K}^{-1} \text{ mol}^{-1} = -12.125 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Neglecting the terms for the temperature dependence of the reaction entropy gives:

$$\begin{aligned}\Delta_r G_T^\circ &= \Delta_r G^\circ - \Delta_r S^\circ (T - T_0) \\ \Delta_r G_{500\text{K}}^\circ &= -300.194 \text{ kJ mol}^{-1} - 11.140 \text{ J K}^{-1} \text{ mol}^{-1} (500.0 \text{ K} - 298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -300.194 \text{ kJ mol}^{-1} - 2.2486 \text{ kJ mol}^{-1} = -302.4426 \text{ kJ mol}^{-1}\end{aligned}$$

The more exact expression gives:

$$\begin{aligned}\Delta_r G_T^\circ &= \Delta_r G^\circ - \Delta_r S^\circ (T - T_0) + \Delta_r C_p^\circ (T - T_0) - \Delta_r C_p^\circ T \ln \frac{T}{T_0} \\ &= -302.443 \text{ kJ mol}^{-1} + (-12.125 \text{ J K}^{-1} \text{ mol}^{-1})(500.0 \text{ K} - 298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) - \\ &\quad (-12.125 \text{ J K}^{-1} \text{ mol}^{-1})(500.0 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln \frac{500.0 \text{ K}}{298.15 \text{ K}} \\ &= -302.443 \text{ kJ mol}^{-1} - 2.447 \text{ kJ mol}^{-1} + 3.134 \text{ kJ mol}^{-1} = -301.756 \text{ kJ mol}^{-1}\end{aligned}$$

The difference between the more approximate and more exact results is 0.2%. Notice that the two terms that are proportional to the reaction heat capacity difference roughly cancel. SO₂ is a byproduct of coal combustion, which is processed in clouds to form SO₃ and H₂SO₄. Atmospheric H₂SO₄ contributes to acidification of fresh water lakes and rivers through the formation of acid rain.

33. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

- When a change in state occurs at constant pressure, the increase in the Gibbs energy of the system must equal the decrease in the Gibbs energy of the surroundings.
- The entropy change of the universe is a spontaneity criterion only for isolated systems.
- Gibbs energy is minimized for processes at constant temperature and pressure and no electrical work.
- For a chemical reaction at constant pressure, the changes in Helmholtz and Gibbs energies are identical if the volume of the products is identical to the volume of the reactants.
- For phase transitions, the Gibbs energy change is zero.

Answer: (a). False: Gibbs energy, in general, is not conserved. The Gibbs energy change of the surroundings is not necessarily equal in magnitude and opposite in sign to the Gibbs energy change of the system. The Gibbs energy change of the surroundings, which are at constant temperature and pressure, is just $\Delta G_{\text{surr}} = \Delta H_{\text{surr}} - T_{\text{surr}} \Delta S_{\text{surr}}$ where:

$$\Delta H_{\text{surr}} = q_{\text{surr}} = -q \quad \text{and} \quad \Delta S_{\text{surr}} = q_{\text{surr}}/T_{\text{surr}} = -q/T_{\text{surr}}$$

where q is the heat transfer for the system. If the process for the system is at constant pressure, $q = q_p = \Delta H$ giving:

$$\Delta H_{\text{surr}} = -\Delta H \quad \text{and} \quad \Delta S_{\text{surr}} = -q/T_{\text{surr}} = -\Delta H/T_{\text{surr}} \quad (\text{cst. } P)$$

and then $\Delta G_{\text{surr}} = 0$. Transfers of energy to the surroundings are always reversible, and the surroundings therefore remain at equilibrium, so that $\Delta G_{\text{surr}} = 0$. In other words, the Gibbs energy change of the universe for a process at constant pressure is entirely a property of the system. $\Delta G_{\text{surr}} = 0$ at constant pressure explains why the Gibbs energy is such a useful concept for constant pressure processes. A correct statement for the problem is “only for equilibrium processes is $\Delta G = -\Delta G_{\text{surr}}$, under which conditions $\Delta G = \Delta G_{\text{surr}} = 0$.” Another statement is that “for a constant pressure process, the Gibbs energy of the surroundings is constant.”

(b). False: the entropy change of the universe is always a good spontaneity criterion. The entropy change of the system is a good spontaneity criterion only for isolated systems. A restatement is “the entropy change of the universe is always positive for a spontaneous process.”

(c). Too restrictive: Gibbs energy is minimized at constant temperature and pressure. The change in Gibbs energy can result from chemical, electrical, or any other form of work. Eq. 15.3.11 is explicitly for the case of chemical and electrical work.

(d). True. If the constant pressure restriction was removed, the statement would no longer necessarily be true; at constant volume considering only gas phase reactants and products $\Delta_r G = \Delta_r A + \Delta_r(PV) = \Delta_r A + \Delta_r n_{\text{gas}} RT$, even though the volume is constant.

(e). False: the Gibbs energy change for a phase transition is positive at temperatures below the equilibrium phase transition temperature (e.g. the standard boiling point or melting point) and negative above the equilibrium phase transition temperature. Were the phase transition Gibbs energy always zero, then phase transitions would never be spontaneous. A restatement is “the Gibbs energy for a phase transition is zero at the equilibrium phase transition temperature.”

34. Show that the internal energy change gives the work for an adiabatic process and the enthalpy change gives the maximum non-PV work for an adiabatic constant pressure process.

Answer: In general $\Delta U = q + w$. Consider an adiabatic process, then $q = 0$ and $\Delta U = w$. The work has a PV and non-PV component, w_{net} . For the system in contact with the surroundings as a constant pressure reservoir the PV-work is reversible, $P_{\text{ext}} = P$, and then $w_{\text{max}} = -P \, dV + w_{\text{net}}$. Also at constant pressure, $\Delta H = \Delta U + P\Delta V$. Substituting $\Delta U = q + w$ gives:

$$\Delta H = \Delta U + P\Delta V = q_{\text{rev}} - P \, dV + w_{\text{net}} + P\Delta V = q_{\text{rev}} + w_{\text{net}}$$

For an adiabatic process $q = 0$ giving finally $\Delta H = w_{\text{net}}$.