

Chemistry 431
Problem Set 8
Fall 2023
Solutions

1. Show that

$$\left(\frac{\partial A}{\partial T}\right)_V = \frac{A - U}{T}$$

Answer:

$$dA = -SdT - PdV$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$A = U - TS$$

$$-S = \frac{A - U}{T}$$

Then

$$\left(\frac{\partial A}{\partial T}\right)_V = \frac{A - U}{T}$$

2. The density of lithium metal is 0.53 g ml^{-1} . Assuming lithium to be incompressible, calculate ΔG when the pressure on 5.0 g of lithium is raised isothermally from 1.0 to 100.0 bar.

Answer:

$$dG = -SdT + VdP$$

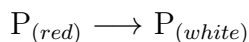
$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\Delta G = \int_{P_1}^{P_2} VdP \cong V\Delta P$$

$$V = \frac{10^{-3} \text{ L}}{0.53 \text{ g}}(5.0 \text{ g}) = 0.00943 \text{ L}$$

$$\Delta G = (0.00943 \text{ L})(99 \text{ bar}) \left(\frac{8.3144 \text{ J}}{0.08314 \text{ L bar}}\right) = 93.36 \text{ J}$$

3. The element phosphorous occurs in two solid phases often called red and white phosphorous. At 25.°C and 1.0 bar pressure, the process



has $\Delta_{r,m}G^{\ominus} = -12134. \text{ J mol}^{-1}$ and $\Delta_{r,m}H_m^{\ominus} = -17573. \text{ J mol}^{-1}$. Assuming the enthalpy change for the process to be temperature independent, at what temperature are the two phases in equilibrium at 1.0 bar pressure?

Answer:

$$\frac{\Delta_{r,m}G^{\ominus}(T_2)}{T_2} - \frac{\Delta_{r,m}G^{\ominus}(T_1)}{T_1} = \Delta H_{r,m}^{\ominus} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

At equilibrium $\Delta G_{r,m}^{\ominus}(T_2) = 0$. Then

$$\begin{aligned} \frac{1}{T_2} - \frac{1}{T_1} &= -\frac{\Delta G_{r,m}^{\ominus}(T_1)}{T_1 \Delta_{r,m}H} \\ \frac{1}{T_2} &= \frac{1}{298 \text{ K}} - \frac{12134}{17573(298 \text{ K})} \\ T_2 &= 963 \text{ K} \end{aligned}$$

4. At 298K the standard enthalpy of formation of diamond is 1.89 kJ mol⁻¹ and the standard free energy of formation of diamond is 2.90 kJ mol⁻¹. The densities of diamond and graphite are respectively 3.52 kg L⁻¹ and 2.25 kg L⁻¹. Calculate the pressure at which diamond and graphite are in equilibrium at a temperature of 0.0°C. Assume the enthalpy of formation of diamond is temperature independent and the densities of both phases are incompressible.

Answer:

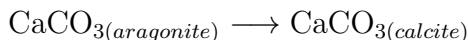
$$\begin{aligned} \frac{\Delta_{f,m}G^{\ominus}(T_2)}{T_2} - \frac{\Delta_{f,m}G^{\ominus}(T_1)}{T_1} &= \Delta_{f,m}H^{\ominus} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \frac{\Delta_{f,m}G^{\ominus}(273)}{273 \text{ K}} - \frac{2900 \text{ J mol}^{-1}}{298 \text{ K}} &= 1890. \text{ J mol}^{-1} \left(\frac{1}{273 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\ \Delta_{m,f}G^{\ominus}(273 \text{ K}) &= 2815. \text{ J mol}^{-1} \\ \Delta_{f,m}G(P) - \Delta_{f,m}G^{\ominus} &= \Delta V_m(P - 1 \text{ bar}) \end{aligned}$$

At pressure P , $\Delta G_{f,m} = 0$ and

$$-2815 \text{ J mol}^{-1} \left(\frac{0.0831 \text{ L bar}}{8.3144 \text{ J}} \right) = (12.00 \text{ g mol}^{-1}) \left(\frac{\text{L}}{3520. \text{ g}} - \frac{\text{L}}{2250. \text{ g}} \right) (P - 1 \text{ bar})$$

$$P = 14630 \text{ bar}$$

5. Calcium carbonate occurs in two solid forms called aragonite and calcite. For the transformation at 298K and 1 bar pressure



$\Delta_{r,m}G^\ominus = -793.8 \text{ J mol}^{-1}$, the density of aragonite is 2.93 kg L^{-1} and the density of calcite is 2.71 kg L^{-1} . Calculate the pressure at which calcite and aragonite are in equilibrium at 298K.

Answer:

$$\Delta_{r,m}G(P) - \Delta_{r,m}G^\ominus = \Delta V_m(P - 1 \text{ bar})$$

At equilibrium $\Delta_{r,m}G = 0$. Then

$$0 + 793.8 \text{ J mol}^{-1} \left(\frac{0.08314 \text{ L bar}}{8.3144 \text{ J}} \right) = \left(\frac{L}{2710 \text{ g}} - \frac{L}{2930 \text{ g}} \right) \left(\frac{100.08 \text{ g}}{\text{mol}} \right) (P - 1 \text{ bar})$$

$$P = 2864 \text{ bar}$$

6. Solid sulfur exists in two crystalline forms; rhombic and monoclinic sulfur. At 1 bar pressure and 298K the thermodynamically most stable phase is rhombic sulfur. At 298K the Gibbs free energy of formation of monoclinic sulfur is 100 J mol^{-1} and the enthalpy of formation of monoclinic sulfur is 330 J mol^{-1} . Assuming the enthalpy of formation of sulfur to be temperature independent, calculate the temperature at which monoclinic and rhombic sulfur are in equilibrium at 1 bar pressure.

Answer:

$$\frac{\Delta_{f,m}G^\ominus(T_2)}{T_2} - \frac{\Delta_{f,m}G^\ominus(T_1)}{T_1} = \Delta_{f,m}H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

At equilibrium

$$\Delta_{f,m}G^\ominus(T_2) = 0$$

Then

$$0 - \frac{100 \text{ J mol}^{-1}}{298 \text{ K}} = 330 \text{ J mol}^{-1} \left(\frac{1}{T_2} - \frac{1}{298 \text{ K}} \right)$$

$$T_2 = 428 \text{ K}$$

7. The most stable form of the element tin (Sn) at 298K and standard 1 bar pressure is a metallic solid and is often called white tin. Gray tin is another solid form of the element that has a diamond crystal lattice and is non metallic. The density of white tin is 7.365 g cm^{-3} , the density of gray tin is 5.769 g cm^{-3} , the standard enthalpy of formation of gray tin is $\Delta_{f,m}H^\ominus = -2.1 \text{ kJ mol}^{-1}$ at 298K and the standard Gibbs free energy of formation of gray tin is $\Delta_{f,m}G^\ominus = 0.10 \text{ kJ mol}^{-1}$ at 298K. Calculate the temperature at which white and gray tin are in equilibrium with each other at a total pressure of 200. bar. You should assume the enthalpy of formation of gray tin is temperature and pressure independent and the densities of both forms of tin are

independent of temperature and pressure.

Answer:

$$\begin{aligned}\Delta_{f,m}G(P_2) - \Delta_{f,m}G^\ominus(P_1) &= \Delta V_{r,m}(P_2 - P_1) \\ \Delta G_{f,m}(200. \text{ bar}) &= (100. \text{ J mol}^{-1}) \left(\frac{0.08314 \text{ L bar}}{8.3144 \text{ J}} \right) \\ + \left(\frac{\text{cm}^3}{5.769 \text{ g}} - \frac{\text{cm}^3}{7.365 \text{ g}} \right) \left(\frac{\text{L}}{1000. \text{cm}^3} \right) \left(\frac{118.7 \text{ g}}{\text{mol}} \right) (200. \text{ bar} - 1 \text{ bar}) &= 1.89 \text{ L bar mol}^{-1} = 189. \text{ J mol}^{-1} \\ \frac{\Delta_{f,m}G(T_2)}{T_2} - \frac{\Delta_{f,m}G(T_1)}{T_1} &= \Delta_{f,m}H \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \Delta_{f,m}G(T_2) &= 0 \\ -\frac{189 \text{ J mol}^{-1}}{298. \text{ K}} &= -2100 \text{ J mol}^{-1} \left(\frac{1}{T_2} - \frac{1}{298. \text{ K}} \right) \\ T_2 &= 273. \text{ K}\end{aligned}$$

8. Consider the process for the formation of gas-phase water from liquid water



At 298. K, the standard Gibbs free energies of formation of liquid and gas-phase water are respectively $\Delta_{f,m}G^\ominus(\text{H}_2\text{O}_{(\ell)}) = -237.1 \text{ kJ mol}^{-1}$ and $\Delta_{f,m}G^\ominus(\text{H}_2\text{O}_{(g)}) = -228.6 \text{ kJ mol}^{-1}$. Given that gas-phase and liquid-phase water are in equilibrium with each other under standard conditions of pressure at 373. K, calculate $\Delta_{r,m}G^\ominus$ for the process given in Eq. (1) at 323. K assuming the enthalpy change for the process is independent of temperature.

Answer:

$$\Delta_{r,m}G^\ominus = \Delta_{f,m}G^\ominus(\text{H}_2\text{O}_{(g)}) - \Delta_{f,m}G^\ominus(\text{H}_2\text{O}_{(\ell)}) = -228.6 \text{ kJ mol}^{-1} - (-237.1 \text{ kJ mol}^{-1}) = 8.5 \text{ kJ mol}^{-1}$$

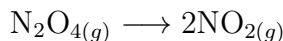
$$\frac{\Delta_{r,m}G^\ominus(T_2)}{T_2} - \frac{\Delta_{r,m}G^\ominus(T_1)}{T_1} = \Delta_{r,m}H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta_{r,m}G^\ominus(373 \text{ K}) = 0$$

$$0 - \frac{8.5 \text{ kJ mol}^{-1}}{298 \text{ K}} = \Delta_{r,m}H^\ominus \left(\frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}} \right) \quad \Delta_{r,m}H^\ominus = 42.3 \text{ kJ mol}^{-1}$$

$$\frac{\Delta_{r,m}G^\ominus(323)}{323 \text{ K}} - \frac{8.5 \text{ kJ mol}^{-1}}{298 \text{ K}} = 42.3 \text{ kJ mol}^{-1} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right) \quad \Delta_{r,m}G^\ominus(323 \text{ K}) = 5.7 \text{ kJ mol}^{-1}$$

9. The standard molar enthalpy and Gibbs free energy changes for the reaction



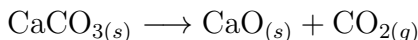
at 298 K are respectively $\Delta_{r,m}H^\ominus = 55.3 \text{ kJ mol}^{-1}$ and $\Delta_{r,m}G^\ominus = 2.80 \text{ kJ mol}^{-1}$. Assuming the enthalpy change is temperature independent, calculate the temperature at which

$$\Delta_{r,m}G^\ominus = -2.80 \text{ kJ mol}^{-1}.$$

Answer:

$$\begin{aligned} \frac{\Delta_{r,m}G^\ominus(T_2)}{T_2} - \frac{\Delta_{r,m}G^\ominus(T_1)}{T_1} &= \Delta_{r,m}H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \frac{-2.80 \text{ kJ mol}^{-1}}{T} - \frac{2.80 \text{ kJ mol}^{-1}}{298 \text{ K}} &= 55.3 \text{ kJ mol}^{-1} \left(\frac{1}{T} - \frac{1}{298 \text{ K}} \right) \\ \frac{58.1}{T} &= 0.176 \text{ K}^{-1} \\ T &= 330 \text{ K} \end{aligned}$$

10. For the reaction

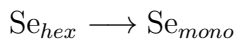


$\Delta_{r,m}G^\ominus = 131.1 \text{ kJ mol}^{-1}$ at 25.0° and $\Delta_{r,m}G^\ominus = 129.5 \text{ kJ mol}^{-1}$ at 30.0°C . Assuming the enthalpy change for the reaction is temperature independent, calculate the change in the Gibbs free energy for the reaction at 50.0°C .

Answer:

$$\begin{aligned} \frac{\Delta_{r,m}G^\ominus(T_2)}{T_2} - \frac{\Delta_{r,m}G^\ominus(T_1)}{T_1} &= \Delta_{r,m}H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \frac{129.5 \text{ kJ mol}^{-1}}{303. \text{ K}} - \frac{131.1 \text{ kJ mol}^{-1}}{298. \text{ K}} &= \Delta_{r,m}H^\ominus \left(\frac{1}{303 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\ \Delta_{r,m}H^\ominus &= 226.4 \text{ kJ mol}^{-1} \\ \frac{\Delta_{r,m}G^\ominus(323 \text{ K})}{323 \text{ K}} - \frac{131.1 \text{ kJ mol}^{-1}}{298 \text{ K}} &= 226.4 \text{ kJ mol}^{-1} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\ \Delta_{r,m}G^\ominus &= 123.1 \text{ kJ mol}^{-1} \end{aligned}$$

11. The element selenium naturally occurs in two crystalline phases; hexagonal (the most stable standard state at 298K) and monoclinic. At 298K the standard enthalpies and Gibbs free energies of formation of monoclinic selenium are respectively $\Delta_{f,m}H^\ominus = 5.549 \text{ kJ mol}^{-1}$ and $\Delta_{f,m}G^\ominus = 5.442 \text{ kJ mol}^{-1}$, and the densities of hexagonal and monoclinic selenium are respectively $\rho_{hex} = 4.819 \text{ g cm}^{-3}$ and $\rho_{mono} = 4.401 \text{ g cm}^{-3}$. Calculate $\Delta_{r,m}G$ for the reaction



at $T = 450. \text{K}$ and $P = 1000. \text{ bar}$. You should assume the densities and enthalpies of formation of both phases are independent of temperature and pressure.

Answer:

$$\frac{\Delta_{f,m}G^\ominus(T_2)}{T_2} - \frac{\Delta_{f,m}G^\ominus(T_1)}{T_1} = \Delta_{f,m}H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\begin{aligned} \frac{\Delta_{f,m}G^\ominus(450)}{450 \text{ K}} - \frac{5442 \text{ J mol}^{-1}}{298 \text{ K}} &= 5549 \text{ J mol}^{-1} \left(\frac{1}{450 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\ \Delta_{f,m}G^\ominus(450) &= 5387 \text{ J mol}^{-1} \\ \Delta_{r,m}G(P_2) - \Delta_{r,m}G(P_1) &= \Delta V_{r,m}(P_2 - P_1) \\ \Delta_{r,m}G(1000) - 5387 \text{ J mol}^{-1} &= \left(\frac{\text{cm}^3}{4.401 \text{ g}} - \frac{\text{cm}^3}{4.819 \text{ g}} \right) \left(\frac{\text{L}}{10^3 \text{ cm}^3} \right) \left(\frac{78.69 \text{ g}}{\text{mol}} \right) \left(\frac{8.3144 \text{ J}}{0.08314 \text{ L bar}} \right) \\ &\quad \times (1000 \text{ bar} - 1 \text{ bar}) \\ \Delta_{r,m}G(2000) &= 5542 \text{ J mol}^{-1} \end{aligned}$$

12. At 1.00 bar pressure and 298K the element tin occurs in two crystal structures often called white and gray tin. White tin is the most stable standard state of the element at 298K and for gray tin $\Delta_{f,m}G^\ominus = 0.10 \text{ kJ mol}^{-1}$. At 1.00 bar pressure gray and white tin are in equilibrium with each other at 284 K, and at 200. bar pressure the two crystal structures are in equilibrium at 272 K. Assuming both gray and white tin to be incompressible, and assuming the molar volumes to be temperature independent, calculate the difference in the molar volume of the two crystal structures of tin.

Answer:

$$\begin{aligned} \frac{\Delta_{f,m}G^\ominus(T_2)}{T_2} - \frac{\Delta_{f,m}G^\ominus(T_1)}{T_1} &= \Delta_{f,m}H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \frac{0}{284 \text{ K}} - \frac{0.10 \text{ kJ mol}^{-1}}{298 \text{ K}} &= \Delta_{f,m}H^\ominus \left(\frac{1}{284 \text{ K}} - \frac{1}{298 \text{ K}} \right) \quad \Delta_{f,m}H^\ominus = -2.02 \text{ kJ mol}^{-1} \end{aligned}$$

At 1 bar pressure

$$\begin{aligned} \frac{\Delta_{f,m}G^\ominus(272)}{272 \text{ K}} - \frac{100 \text{ J mol}^{-1}}{298 \text{ K}} &= -2020 \text{ J mol}^{-1} \left(\frac{1}{272 \text{ K}} - \frac{1}{298 \text{ K}} \right) \quad \Delta_{f,m}G^\ominus(272) = -85.0 \text{ J mol}^{-1} \\ \Delta_{f,m}G(200. \text{ bar}) - \Delta_{f,m}G^\ominus(1 \text{ bar}) &= \Delta V_m(200. \text{ bar} - 1 \text{ bar}) \\ 0 + 85.0 \text{ J mol}^{-1} \left(\frac{0.083144 \text{ L bar}}{8.3144 \text{ J}} \right) &= \Delta V_m(200. \text{ bar} - 1.00 \text{ bar}) \\ \Delta V_m &= 4.27 \times 10^{-3} \text{ L mol}^{-1} \end{aligned}$$

13. Solid and liquid mercury are in equilibrium with each other at 234 K and 1.00 bar pressure. Given the enthalpy of fusion of solid mercury is $\Delta_{fus,m}H^\ominus = 2.29 \text{ kJ mol}^{-1}$ is independent of temperature and pressure, and given the densities of solid and liquid mercury are respectively $\rho_{solid} = 14.18 \text{ g cm}^{-3}$ and $\rho_{liquid} = 13.69 \text{ g cm}^{-3}$ also independent of temperature and pressure, calculate $\Delta_{r,m}G$ for the transition from solid to liquid mercury at 298 K and 200. bar pressure.

Answer:

At 1.00 bar

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$0 - \frac{\Delta_{fus,m}G(298)}{298} = 2290 \text{ J mol}^{-1} \left(\frac{1}{234} - \frac{1}{298} \right) \quad \Delta_{fus,m}G = -626 \text{ J mol}^{-1}$$

At 200 bar

$$\begin{aligned} \Delta_{fus,m}G(P_2) - \Delta_{fus,m}G(P_1) &= \Delta V \Delta P \\ \Delta_{fus,m}G(200.) &= -626 \text{ J mol}^{-1} \\ + \left(\frac{\text{cm}^3}{13.69 \text{ g}} - \frac{\text{cm}^3}{14.18 \text{ g}} \right) \left(\frac{200.6 \text{ g}}{\text{mol}} \right) \left(\frac{\text{L}}{10^3 \text{ cm}^3} \right) (199 \text{ bar}) \left(\frac{8.3144 \text{ J}}{0.083144 \text{ L bar}} \right) \\ &= -616 \text{ J mol}^{-1} \end{aligned}$$

14. A 1.0 liter vessel containing neon at 25.°C and 1.0 bar pressure is connected to a 5.0 liter vessel containing nitrogen gas at 25.°C and 1.0 bar pressure. If the gases are allowed to diffuse into each other adiabatically, calculate ΔG and ΔS for the process.

Answer:

$$n_{Ne} = \frac{PV}{RT} = \frac{(1 \text{ bar})(1 \text{ L})}{(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 0.0404 \text{ mol}$$

$$n_{N_2} = \frac{(1 \text{ bar})(5 \text{ L})}{(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 0.202 \text{ mol}$$

$$\chi_{Ne} = \frac{0.0404}{0.0404 + 0.202} = 0.167$$

$$\chi_{N_2} = 1 - \chi_{Ne} = 0.833$$

$$n_{tot} = 0.202 \text{ mol} + 0.0404 \text{ mol} = 0.2424 \text{ mol}$$

$$\begin{aligned} \Delta G &= nRT[\chi_{Ne} \ln \chi_{Ne} + \chi_{N_2} \ln \chi_{N_2}] \\ &= (0.242 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})[0.833 \ln 0.833 + 0.167 \ln 0.167] = -270.9 \text{ J} \end{aligned}$$

$$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_P = - \frac{270.9 \text{ J}}{298 \text{ K}} = 0.91 \text{ J K}^{-1}$$

15. 1.0 moles each of Ne and Ar gas at 1 bar pressure and a temperature of 298K form a homogeneous ideal gas mixture isothermally at constant pressure. Calculate the minimum work required to separate the two gases to produce two separate containers of each gas at 1 bar pressure and 298K.

Answer:

$$\begin{aligned} \Delta G &= nRT \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \\ &= 2RT \ln 0.5 = (2 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln 0.5 = -3435 \text{ J} \end{aligned}$$

Notice that

$$\Delta A = \Delta G - \Delta(PV) = \Delta G - \Delta(nRT) = \Delta G$$

Then the total reversible work required is at least 3435 J.