

Chapter 14 Problems: Focusing on Chemical Reactivity

1. Find the number of thermodynamic constituents and components for a solution of hexane and chloroform. Find the expression for dG for changes in the number of components in an open system at constant temperature and pressure.

Answer: The number of constituents and components is the same since there are no chemical reactions or chemical constraints. There are no chemical constraints because there are no special chemical conditions relating the amounts of each constituent. There are two components, which can be expressed as n_h for hexane and n_c for chloroform. At constant temperature and pressure:

$$dG = \mu_h dn_h + \mu_c dn_c$$

2. Lime is made commercially through the thermal decomposition of limestone, which is composed primarily of calcium carbonate:



Find the number of thermodynamic components starting with only CaCO_3 . In other words, assume that there are no other sources of CaO or CO_2 other than the decomposition of CaCO_3 .

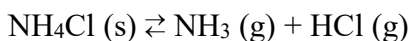
Answer: There are three constituents: CaCO_3 , CaO , and CO_2 . So $n_s = 3$. However, there is one chemical reaction and one chemical constraint. The chemical constraint is that the initial reaction is prepared from just CaCO_3 with no other sources of the products than the chemical reaction. The number of components is then given by Eq. 14.2.1:

$$\begin{aligned} c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 3 - 1 - 1 = 1 \end{aligned}$$

Once the system attains equilibrium the amounts of products can be obtained from the equilibrium expression: the partial pressure of CO_2 at equilibrium is given by:

$$K_p = P_{\text{CO}_2}.$$

3. Solid ammonium chloride decomposes at high temperatures to give ammonia and hydrogen chloride gas:



Find the number of components for a system prepared from only $\text{NH}_4\text{Cl} (\text{s})$.

Answer: There are three constituents: $\text{NH}_4\text{Cl} (\text{s})$, $\text{NH}_3 (\text{g})$, and $\text{HCl} (\text{g})$. However, there is one chemical reaction and one chemical constraint. The chemical constraint is that the initial reaction is prepared from just $\text{NH}_4\text{Cl} (\text{s})$ with no other sources of the products than the chemical reaction.

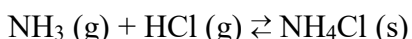
$$\begin{aligned}c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 3 - 1 - 1 = 1\end{aligned}$$

At equilibrium the amounts of reactants and products can be obtained from the equilibrium expression:

$$K_p = P_{\text{NH}_3} P_{\text{HCl}}$$

Since the only source of products is the chemical reaction and from the 1:1 stoichiometry, $P_{\text{NH}_3} = P_{\text{HCl}}$.

4. Gas phase ammonia and hydrogen chloride gas react to form solid ammonium chloride:



(a). Find the number of components for a system prepared from arbitrary amounts of NH_3 and HCl . (b). Find the number of components for a system prepared from equal-molar amounts of NH_3 and HCl .

Answer: There are three constituents: NH_3 (g), HCl (g), and NH_4Cl (s). There is one chemical reaction. For (a) there are no additional chemical constraints and from Eq. 14.2.1:

$$\begin{aligned}c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 3 - 1 - 0 = 2\end{aligned}$$

For (b) the specification of equal-molar amounts of reactants is a chemical constraint and then the number of components is given by:

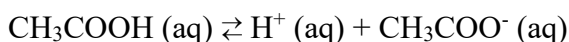
$$\begin{aligned}c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 3 - 1 - 1 = 1\end{aligned}$$

The information from the chemical reactions is algebraically expressed by the equilibrium expressions. At equilibrium the amounts of reactants and products can be obtained from the equilibrium expression:

$$K_p = \frac{1}{P_{\text{NH}_3} P_{\text{HCl}}}$$

and since the reactants are supplied in equal-molar amounts and the reaction stoichiometry is 1:1, $P_{\text{NH}_3} = P_{\text{HCl}}$. This problem is just the reverse of Problem 3; but as always we should get the same result since at equilibrium every chemical reaction is reversible. It shouldn't matter what direction the reaction is written, from the point of view of the number of components. K_p in this problem is equal to $1/K_p$ in Problem 3.

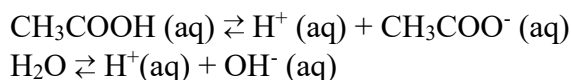
5. Consider the dissociation of the weak acid, acetic acid, in aqueous solution:



Find the number of constituents and thermodynamic components starting with only acetic acid and water. In other words, assume that there are no other sources of CH_3COO^- other than the

dissociation of CH_3COOH . Also, include the dissociation of water as a source of H^+ . Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

Answer: The number of constituents is five: CH_3COOH , H^+ , CH_3COO^- , OH^- , and H_2O . The solution is made from acetic acid and water, so the number of components is 2. There are two chemical reactions, the dissociation of acetic acid and water:



and then the number of chemical constraints is one, as is given by:

$$\begin{aligned}c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 5 - 2 - 1 = 2\end{aligned}$$

Charge balance is the chemical constraint:

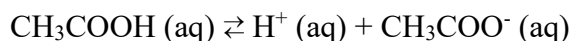
$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] + [\text{OH}^-]$$

The two components are most easily expressed as the mole amounts of CH_3COOH and H_2O , although the choice is not unique.

The information from the chemical reactions is algebraically expressed by the equilibrium expressions. At equilibrium the amounts of reactants and products can be obtained by solving:

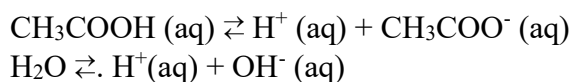
$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{and} \quad K_w = [\text{H}^+][\text{OH}^-].$$

6. Consider the dissociation of the weak acid, acetic acid, in aqueous solution:



Find the number of constituents and thermodynamic components starting with a solution prepared from acetic acid, sodium acetate, and water. Also, include the dissociation of water as a source of H^+ . Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

Answer: Since the solution is prepared from acetic acid and sodium acetate there are two sources of CH_3COO^- , the dissociation of CH_3COOH and added sodium acetate. The sources of H^+ are the dissociation of CH_3COOH and H_2O . The number of constituents is six: CH_3COOH , H^+ , CH_3COO^- , OH^- , Na^+ , and H_2O . The number of components is three, since the solution can be made up from arbitrary amounts of acetic acid, sodium acetate, and water. There are two chemical reactions, the dissociation of acetic acid and water:



Charge balance is the chemical constraint:



The number of thermodynamic chemical components is then:

$$\begin{aligned} c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 6 - 2 - 1 = 3 \end{aligned}$$

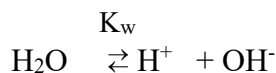
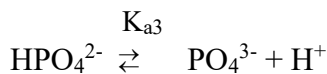
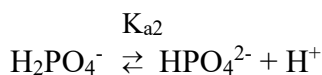
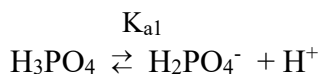
The three components are most easily expressed as the mole amounts of acetic acid, sodium acetate, and H_2O , although the choice is not unique.

The information from the chemical reactions is algebraically expressed by the equilibrium expressions. At equilibrium the amounts of reactants and products can be obtained from the equilibrium expressions:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{and} \quad K_w = [\text{H}^+][\text{OH}^-].$$

7. Find the number of constituents and thermodynamic components starting with a solution prepared from phosphoric acid, sodium hydroxide, and water. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

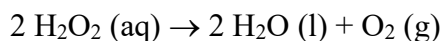
Answer: There are three chemical components, phosphoric acid, sodium hydroxide, and water. There are eight constituents: Na^+ , H^+ , OH^- , H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , and H_2O . The equilibria are:



giving four chemical reactions. With three components and four reactions, there must be only one chemical constraint: $c = 8 - 4 - 1 = 3$. The charge balance is the chemical constraint:

$$[\text{Na}^+] + [\text{H}^+] = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] + [\text{OH}^-]$$

8. Hydrogen peroxide, which is used as a topical disinfectant, decomposes to give O_2 gas in a highly exothermic reaction. This reaction is often used as a rather spectacular chemical demonstration:



Hydrogen peroxide is also important in redox reactions in the environment and in biological processes. During this reaction many things can change: V, P, S, T, U, H, and the mole amounts

of the reactants and products. Keeping track of all these variables can be daunting. How can we simplify the definition of our system so that we can focus on the chemical changes?

Answer: One possibility to study this reaction is as follows.

Step 1: The reaction is set up in a closed piston initially containing only the H_2O_2 solution so that the only source of $\text{O}_2(\text{g})$ is from the decomposition of the hydrogen peroxide. Therefore, there is only one chemical component and this quantity is fixed by the closed system. There are three dependent chemical constituents, H_2O_2 , H_2O , and O_2 :

$$dU = TdS - PdV + 2 \mu_{\text{H}_2\text{O}} d\xi + \mu_{\text{O}_2} d\xi - 2 \mu_{\text{H}_2\text{O}_2} d\xi \quad 1.$$

However, there is only one composition variable, ξ , because there is one chemical reaction. Starting with reactants only, if the reaction were to go to completion, ξ ranges from 0 to 1 mol. In the final equilibrium state, the extent of the reaction will also be constrained to the equilibrium value with $\xi < 1$.

Step 2: Consider the closed chemical reaction as a system which is held at constant temperature and pressure by contact with the surroundings. The surroundings are large in extent so that the surroundings act as a constant temperature and pressure reservoir. Therefore the temperature and pressure in Eq. 1 are constrained: $T = T_{\text{surr}}$, $P = P_{\text{ext}}$. In other words, the T and P in Eq. 1 are not independent variables.

Step 3: The composite of the system and surroundings is assumed to be isolated. Therefore,

$$\begin{aligned} \delta q &= -\delta q_{\text{surr}}, \quad dw = -dw_{\text{surr}} \\ dV_{\text{tot}} &= dV + dV_{\text{surr}} = 0, \quad \text{giving } dV = -dV_{\text{surr}}, \\ dU_{\text{tot}} &= dU + dU_{\text{surr}} = 0, \quad \text{giving } dU = -dU_{\text{surr}} \end{aligned}$$

9. For the reaction in the last problem, evaluate the change in entropy of the system, the surroundings, and the total change in entropy. Don't use any specific numbers; just consider the appropriate equations and inequalities. Compare the results for the entropy with the results from the last problem for the change in internal energy.

Answer: The entropy change for the system is dS . The entropy change in the surroundings is always straightforward; from Eq. 12.5.2:

$$dS_{\text{surr}} = \frac{\delta q_{\text{surr}}}{T_{\text{surr}}} = \frac{-\delta q}{T} \quad 1$$

and since the system is at constant pressure, Eq. 12.5.4, $\delta q = \delta q_p$:

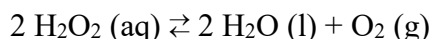
$$dS_{\text{surr}} = \frac{\delta q_{\text{surr}}}{T_{\text{surr}}} = \frac{-dH}{T} \quad 2$$

However, entropy is not conserved for a spontaneous process:

$$dS_{\text{tot}} = dS + dS_{\text{surr}} > 0 \quad 3$$

The inequality is from the Second Law. For the internal energy, $dU_{\text{tot}} = dU + dU_{\text{surr}} = 0$ because the internal energy is conserved. Equations 1-3 are the basis for the next chapter.

10. The decomposition of hydrogen peroxide is a spontaneous process:

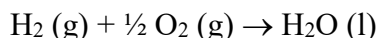


How can we use thermodynamics, which only applies to systems at equilibrium, to study this process?

Answer: To calculate the change in internal energy, enthalpy, entropy, and as we shall see Gibbs energy for the reaction, we consider a temporary internal constraint that prevents the reaction from occurring. Then the changes ΔU , ΔH , ΔS , and ΔG can be calculated from the state of the system before and after the internal constraint is removed.

Since there is only one reactant for this reaction you might be wondering how we might establish such an internal constraint. One way is to measure the properties of the hydrogen peroxide in a long enough time interval after it has been placed in the closed piston that the initial equilibrium state can be established, but before the reaction has had a chance to proceed to an appreciable extent. For such a short time interval, the system can be considered as at equilibrium with respect to temperature and pressure gradients, but not at equilibrium with respect to the overall course of the chemical reaction. However, this reaction is slow in the absence of a catalyst. Hydrogen peroxide can be purchased in drug stores for this reason. The kinetic stability of this metastable system acts as a *de facto* internal constraint. So the properties of the hydrogen peroxide solution would be measured and then a catalyst would be added to accelerate the attainment of equilibrium. If you have ever seen this reaction as a lecture demonstration, the catalyst that is used is solid MnO.

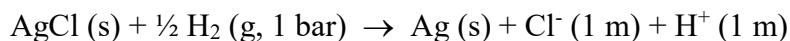
11. Consider the following chemical reaction at room temperature and in the absence of a catalyst:



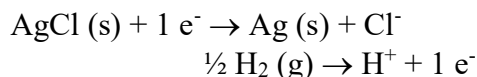
This reaction is spontaneous and therefore the process is irreversible. This reaction is in fact the primary source of propulsion for the space shuttle. Describe how we can apply thermodynamics to calculating the change in internal energy and entropy for this process when the reaction goes to equilibrium by an irreversible reaction.

Answer: The reaction of H_2 and O_2 at room temperature and in the absence of a catalyst is very slow. A mixture of H_2 and O_2 is metastable at room temperature. The kinetic stability of this metastable system acts as a temporary internal constraint. It is very easy to measure the properties of a mixture of H_2 and O_2 , giving U_1 and S_1 . After addition of a catalyst (a piece of Pt metal) the reaction quickly proceeds to equilibrium and then the final U_2 and S_2 can be measured. Then $\Delta U = U_2 - U_1$ and $\Delta S = S_2 - S_1$.

12. Devise an internal constraint for an electrochemical reaction that you wish to maintain at the initial conditions. For example consider the reaction:



Answer: The application of an external voltage to the electrochemical cell that is equal to the initial emf maintains the initial conditions in the cell. The electrochemical reaction can be broken into two half-cells:



The electrochemical cell: $\text{Pt} | \text{H}_2 \text{ (g)} | \text{H}^+ \text{ (1 m)}, \text{Cl}^- \text{ (1 m)} | \text{AgCl (s)} | \text{Ag(s)}$ has a cell potential (the standard state cell potential) of $E = 1.223 \text{ V}$. If a battery with a voltage of 1.223 V were attached to this electrochemical cell, the cell would be at equilibrium and no AgCl (s) would react. After removing the battery and connecting the cell electrodes with a wire, the reaction will reach equilibrium with increased H^+ and Cl^- concentrations with a final cell emf of 0 V . $\Delta_r G = -nFE$ for this reaction, even though the course of the reaction is very irreversible.

An even easier way to arrange for a temporary internal constraint is to simply leave the electrodes unconnected. However, we wouldn't be able to experimentally measure the initial voltage of the system. Stated in other terms, an unused battery maintains its initial voltage.

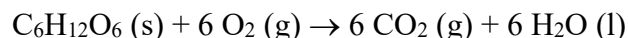
13. Determine the change in internal energy for a reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:



Answer:

$$dU = TdS - PdV + \mu_{\text{NH}_3} d\xi - \frac{1}{2} \mu_{\text{N}_2} d\xi - \frac{3}{2} \mu_{\text{H}_2} d\xi$$

14. Determine the change in internal energy for a reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:

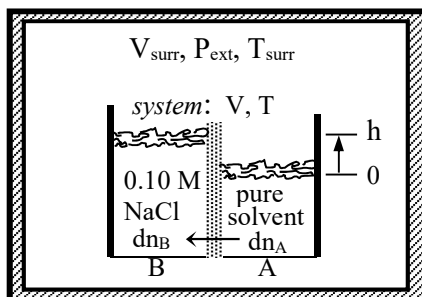


Answer:

$$dU = TdS - PdV + 6 \mu_{\text{H}_2\text{O}} d\xi + 6 \mu_{\text{CO}_2} d\xi - \mu_{\text{C}_6\text{H}_{12}\text{O}_6} d\xi - 6 \mu_{\text{O}_2} d\xi$$

15. A 0.10 M NaCl aqueous solution is separated from pure water by a semi-permeable membrane. The height difference between the solution and the pure solvent is h and the corresponding equilibrium osmotic pressure is π . The system and the surroundings are in equilibrium. Assume the molar volume of the solvent in the solution is essentially the pure molar volume. Construct a isolated composite system with this membrane system and the surroundings. Consider the transfer of dn_A moles of solvent from the pure solvent through the membrane into the solution. Consider $h = 0$ as the reference height. Relate P_{ext} and T_{surr} with P_A , P_B , and T , where P_A is the pressure at $h = 0$ for the pure solvent and P_B is the pressure at $h = 0$ for the NaCl

solution. Relate dU , δq , δw , and dV for the total composite, the surroundings, the system (A and B), and for the pure solvent (A) and the NaCl solution (B).



Answer: The system is closed with no exchange of matter between the system and the surroundings (no evaporation of the solvent). The exchange of energy between the system and surroundings is restricted to transfers of heat and PV-work. Let the pure solvent compartment be side A and the NaCl solution be side B with:

$$\delta q = \delta q_A + \delta q_B \quad \delta w = \delta w_A + \delta w_B \quad \text{and} \quad dU = dU_A + dU_B$$

The surroundings act as a constant temperature and pressure reservoir with $T_{\text{surr}} = T = 298.2 \text{ K}$. The compartment pressures are $P_A = P_{\text{ext}} = 1.00 \text{ bar}$ and $P_B = P_{\text{ext}} + \pi$. The composite is isolated giving:

$$\begin{aligned} dU_{\text{tot}} &= 0 & dU &= dU_A + dU_B = -dU_{\text{surr}} \\ \delta q_{\text{tot}} &= 0 & \delta q &= \delta q_A + \delta q_B = -\delta q_{\text{surr}} \\ \delta w_{\text{tot}} &= 0 & \delta w &= \delta w_A + \delta w_B = -\delta w_{\text{surr}} \\ dV_{\text{tot}} &= 0 & dV &= dV_A + dV_B = -dV_{\text{surr}} \end{aligned}$$

In other words, the total internal energy is conserved. The membrane acts as a temporary constraint. Assuming the molar volume of the solvent is the same on both sides of the membrane gives $dV_B = -dV_A$. There is no net change in volume of the system or surroundings:

$$dV = dV_A + dV_B = 0 \quad \text{and} \quad dV_{\text{surr}} = 0$$

16. (Challenge Problem) For the previous problem, find the PV-work, δw , for the transfer of dn_A moles of solvent from the pure solvent through the membrane into the NaCl solution.

Answer: The plan is to evaluate the PV-work in each compartment separately and then add the results to find the net work for the system.

In the transfer of dn_A moles of solvent from the A compartment into the B compartment, the surroundings does work on the A compartment, in compression at P_{ext} , and the system does work on the surroundings in the B compartment, in expansion against $P_{\text{ext}} + \pi$:¹

$$\delta w_A = -P_{\text{ext}} dV_A \quad \delta w_B = -(P_{\text{ext}} + \pi) dV_B = (P_{\text{ext}} + \pi) dV_A$$

The net work for the system is $\delta w = \pi dV_A$. The change in volume is given by:

$$dV_A = -(\partial \mathcal{U}_A / \partial n_A)(1 \times 10^6 \text{ mL} / 1 \text{ m}^3) dn_A$$

where \mathcal{M}_A is the molar mass of the solvent and d_A is the density of the solvent. We will find in the ideal solutions chapter that the energy requirement for the process is supplied by the dilution of the NaCl solution. The reverse of the process described in this problem is called reverse osmosis. Reverse osmosis is commonly used for water purification. The energy requirement for reverse osmosis systems is large and is given by $\delta w = \pi dV_A$.

Literature Cited:

1. S. R. Caplan, A. Essig, *Bioenergetics and Linear Nonequilibrium Thermodynamics*, Harvard University Press, Cambridge, Massachusetts, 1999. Section 2.4.