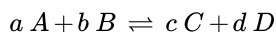


13.2: The Gibbs Free Energy Change for A Reaction of Ideal Gases

Let us consider a system that consists of a mixture of ideal gases A , B , C , and D , at a particular fixed temperature. We suppose that reaction occurs according to



We want to think about what happens when a moles of A (at pressure P_A) and b moles of B (at pressure P_B) react to form c moles of C (at pressure P_C) and d moles of D (at pressure P_D) under conditions in which the partial pressures in the mixture remain constant at P_A , P_B , P_C , and P_D . At first encounter, these conditions may appear to be impossible; if A reacts, its partial pressure must change. However, on reflection, we recognize that by making the system very large, a moles of A and b moles of B can disappear without changing P_A or P_B very much. In fact, we can make the change in P_A and P_B as small as we like just by making the original system large enough. The same considerations apply to P_C and P_D . We let $\Delta_r G$ be the Gibbs free energy change under these conditions. We want to know how the Gibbs free energy of this system, G , and the Gibbs free energy change, $\Delta_r G$, depend on the partial pressures of the gases involved in the reaction.

We have observed repeatedly that the temperature and pressure of a system undergoing spontaneous change may not be well defined, and the concentration of a component may vary from point to point within a given phase. If any of these inhomogeneities are substantial, the reaction conditions in the previous paragraph are not met. On the other hand, if any pressure and temperature variations are too small to have observable effects, and there are no point-to-point concentration variations, it is entirely reasonable to suppose that the Gibbs free energies of the system, and of its individual components, are described by the thermodynamic models we have developed for reversible systems.

To see that there can be no objection in principle to measuring Gibbs free energies in a non-equilibrium system, we need only find a hypothetical equilibrium system whose state functions must have the same values. Thus, if the reaction $a A + b B \rightleftharpoons c C + d D$ does not occur, mixtures of gases A , B , C , and D in any proportions can be at equilibrium, and the thermodynamic properties of any such mixture are well defined. In concept, we can produce a hypothetical equilibrium state equivalent to any intermediate state in the spontaneous process if we suppose that the reaction occurs only in the presence of a solid catalyst. By introducing and then removing the catalyst from the reaction mixture, we can produce a quasi-equilibrium state whose composition is identical to that of the spontaneous reaction at any particular extent of reaction. In this quasi-equilibrium state, the pressure is equal to the applied pressure, and the temperature is equal to that of the surroundings. If the spontaneous uncatalyzed reaction is slow compared to the rate at which the pressure and temperature of the system can equilibrate with the applied pressure and the surroundings temperature, the state functions of a spontaneously reacting system and a static, quasi-equilibrium system with the same composition must be essentially identical.

It turns out that we can find the dependence of $\Delta_r G$ on concentrations by considering a fundamentally different system—one that is composed of exactly the same amount of each of these gases, but in which the gases are not mixed. Each gas occupies its own container. For the partial pressures P_A , P_B , P_C , and P_D , the Gibbs free energies per mole are

$$\bar{G}_A(P_A) = \Delta_f G^\circ(A, P^\circ) + RT \ln p_A$$

$$\bar{G}_B(P_B) = \Delta_f G^\circ(B, P^\circ) + RT \ln p_B$$

$$\bar{G}_C(P_C) = \Delta_f G^\circ(C, P^\circ) + RT \ln p_C$$

$$\bar{G}_D(P_D) = \Delta_f G^\circ(D, P^\circ) + RT \ln p_D$$

The Gibbs free energy of this system, which is just a composite of the separated gases, is

$$G = n_A \bar{G}_A(P_A) + n_B \bar{G}_B(P_B) + n_C \bar{G}_C(P_C) + n_D \bar{G}_D(P_D)$$

If we subtract the Gibbs free energies of a moles of reactant A and b moles of reactant B from the Gibbs free energies of c moles of product C and d moles of product D , we find

$$\begin{aligned} & c \bar{G}_C(P_C) + d \bar{G}_D(P_D) - a \bar{G}_A(P_A) - b \bar{G}_B(P_B) \\ &= c \Delta_f G^\circ(C, P^\circ) + d \Delta_f G^\circ(D, P^\circ) - a \Delta_f G^\circ(A, P^\circ) - b \Delta_f G^\circ(B, P^\circ) + RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b} \end{aligned}$$

To represent these free energy differences when the gases are in separate containers, we introduce the abbreviations

$$\Delta_{sep} G = c \bar{G}_C(P_C) + d \bar{G}_D(P_D) - a \bar{G}_A(P_A) - b \bar{G}_B(P_B)$$

and

$$\Delta_r G^\circ = c \Delta_f G^\circ(C, P^\circ) + d \Delta_f G^\circ(D, P^\circ) - a \Delta_f G^\circ(A, P^\circ) - b \Delta_f G^\circ(B, P^\circ)$$

so that the difference between the Gibbs free energies of the separated reactants and products can be written more compactly as

$$\Delta_{sep} G = \Delta_r G^\circ + RT \ln \frac{P_C P_D}{P_A P_B}$$

$\Delta_{sep} G$ is the difference in the Gibbs free energies when the pressures of the separated gases are fixed at P_A , P_B , P_C , and P_D . Note that, if any of the pressures changes, $\Delta_{sep} G$ changes. When we introduce $\Delta_r G^\circ$ in [Section 11.10](#), we emphasize that this quantity is the difference between the standard Gibbs free energies of the separated products

c moles of C at 1 bar and d moles of D at 1 bar.

and the separated reactants

a moles of A at 1 bar and b moles of B at 1 bar.

We call $\Delta_r G^\circ$ the **standard Gibbs free energy change** for the reaction. At a given temperature, $\Delta_r G^\circ$ is a constant. Our choice of standard state for the Gibbs free energy of a compound means that we can calculate the standard free energy change for a reaction from the standard free energies of formation of the products and reactants:

$$\Delta_r G^\circ = c \Delta_f G^\circ(C, P^\circ) + d \Delta_f G^\circ(D, P^\circ) - a \Delta_f G^\circ(A, P^\circ) - b \Delta_f G^\circ(B, P^\circ)$$

Let us recapitulate: In the first system, we are interested in the Gibbs free energy change, $\Delta_r G$, for a process in which a moles of A and b moles of B are converted to c moles of C and d moles of D in a (large) mixed system where the partial pressures are constant at the values P_A , P_B , P_C , and P_D . In the second system, there is actually no process at all. The Gibbs free energy change, $\Delta_{sep} G$, is merely a computed difference between the Gibbs free energies of the specified quantities of product and reactant gases, where each gas is in its own container at its specified pressure. When the gases are ideal, the Gibbs free energy differences (changes) for these two systems turn out to be the same. That is, $\Delta_{sep} G = \Delta_r G$.

This relationship is valid for systems in which the properties of one substance are not affected by the concentrations of other substances present. It is not true in general. On the other hand, $\Delta_r G^\circ$ is always the computed difference between the standard Gibbs free energies of the pure separated products and reactants. For ideal gases,

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{P_C P_D}{P_A P_B}$$

(reaction of ideal gases)

We have asserted that we can equate $\Delta_{sep} G$ and $\Delta_r G$ for systems composed of ideal gases. Now we need to show that this is true. This is easy if we first understand a related problem—the thermodynamics of mixing ideal gases.

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