> **Example 17.2 Calculation of standard state Gibbs energy of reaction (Continued)**
>
> The equilibrium constant is determined from Eqn. 17.16;
>
> $$\exp\left(\frac{-\Delta G^o_{298.15}}{RT}\right) \;=\; \exp\left(\frac{-79,490}{8.314(298.15)}\right) \;=\; 1.18{\times}10^{-14} \;=\; K_{a,\,298.15}$$
>
> This reaction is not favorable at room temperature because the equilibrium constant is small.

Composition and Pressure Independence of K_a

The use of standard states for calculating ΔG^o_T has important implications on the composition and pressure independence of K_a. The standard state is at a fixed pressure, P°. Thus, ΔG^o_T is independent of pressure. The standard states are also at fixed composition (often pure), and thus ΔG^o_T is independent of equilibrium composition. Looking at Eqn. 17.20, we conclude that because ΔG^o_T is independent of equilibrium composition and pressure, K_a is independent of equilibrium composition and pressure. One important point is that the state of aggregation in the standard state *is* important and the values of ΔG^o_T and K_a do depend on the state of aggregation in the standard state; this point will be clarified in later sections.

The equilibrium constant K_a is independent of composition and pressure.

We have now demonstrated steps 2(a), 3, and 4 for the procedure given in Section 17.1. The concepts have been demonstrated, but we must correct the temperature before doing calculations at temperatures other than 298.15 K. The butadiene reaction of Example 17.2 becomes more favorable with a larger K_a at higher temperatures. We will discuss some important aspects of the effects of pressure and inerts and also discuss reaction spontaneity before showing the calculation of temperature corrections.

17.5 EFFECTS OF PRESSURE, INERTS, AND FEED RATIOS

At a given temperature, equilibrium values of the reaction coordinate are affected by pressure, inerts, and feed ratios. The principle that changing the quantities affects equilibrium conversions is known as **Le Châtelier's principle** in honor of Henry Louis Le Châtelier who first characterized the phenomenon. An understanding of Le Châtelier's principle is important for operating industrial reactions. Two important modifications led to significant hydrogen conversions in Example 17.1 even though the equilibrium constant was small—use of pressure and nonstoichiometric feed.

Henry Louis Le Châtelier (1850–1936) was a French chemist. He was elected to the French Académie des Sciences and the Royal Swedish Academy of Sciences in 1907.

Pressure Effects

Pressure has little effect on the activities of condensed species (e.g., the Poynting correction is typically small) and thus it has a primary significance only for reactions with gas phase components. Pressure has important effects when both 1) gas species are involved in reactions and 2) the stoichiometric numbers of gas species are different for reactants and products. When the stoichiometric moles of gas species are the same for reactants and products, P has no effect by the ideal gas approximation, and for nonideal gases only indirect effects due to fugacity coefficients.

The equilibrium constants for ideal gases can be written

$$\left(\prod y_i^{v_i}\right) P^{\Sigma v_i} = K_a \qquad \text{(ig) 17.21}$$

This form makes the pressure effect more obvious. As mentioned above, when the stoichiometric number of gas moles is the same for products and reactants, $\Sigma v_i = 0$ and the pressure effect drops out. When the stoichiometric numbers of vapor reactant moles is greater than the stoichiometric numbers of product vapor moles, an increase in pressure will drive the reaction to higher conversions,. $\Sigma v_i < 0$. When the stoichiometric gas mole ratios are reversed, a decrease in pressure will help drive the reaction to higher conversions, $\Sigma v_i > 0$. In Example 17.1 the pressure of 20 bar was important to yield significant conversions. It can be helpful to consider that qualitatively the pressure "squeezes" the reaction towards the side with fewer gas moles. As an exercise, determine the reaction coordinate for the same feed when the pressure is 1 bar.
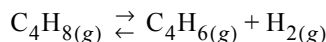
Inerts

A component that does not participate in a reaction is called **inert.** Inert gas components often have an indirect, but important effect on the equilibrium reaction coordinate when gas phase species are present. Inerts change the overall mole fractions and thus mitigate the pressure effects. When $\Sigma v_i > 0$, adding an inert will increase conversion at a fixed total pressure. However, when $\Sigma v_i < 0$, the mitigation of the pressure effect is undesirable and inerts should be avoided. Qualitatively, the presence of an inert decreases the "squeezing" effect mentioned above.

Nonstoichiometric Feed

Conversions of specific reactants are influenced using nonstoichiometric feed. In Example 17.1, excess CO was fed to the reactor; conversions were 42% (H_2), and 10.5% (CO). Generally, an excess of one reactant will tend to increase conversion of the other reactant. The effect can be seen qualitatively using Eqn. 17.2. For a given K_a, at a certain value of y_{CH_3OH}, a higher value of y_{CO} results in a lower value of y_{H_2}. When using stoichiometric feed (CO:H_2 = 1:2) in Example 17.1, the equilibrium conversions of H_2 and CO are equal (40.6%). Example 17.1 includes both excess CO and a pressure effect. The excess CO in Example 17.1 is high enough to mitigate the beneficial pressure effect in a manner similar to an inert gas. The feed ratio giving highest H_2 conversion for the specified conditions uses less excess CO, (CO:H_2 = 1:1), which results in conversions of 45.2% (H_2) and 22.6% (CO). Use of nonstoichiometric feed is common in industrial reactions because in some cases it helps avoid side reactions in addition to effects on equilibrium.

Example 17.3 Butadiene production in the presence of inerts

Consider again the butadiene reaction of Example 17.2 on page 640. Butadiene is prepared by the gas phase catalytic dehydrogenation of 1-butene, at 900 K and 1 bar.

$$C_4H_{8(g)} \overset{\rightarrow}{\leftarrow} C_4H_{6(g)} + H_{2(g)}$$

(a) In order to suppress side reactions, the butene is diluted with steam before it passes into the reactor. Estimate the conversion of 1-butene for a feed consisting of 10 moles of steam per mole of 1-butene.

(b) Find the conversion if the inerts were absent and side reactions are ignored.

(c) Find the total pressure that would be required to obtain the same conversion as in (a) if no inerts were present.