

Chapter 12

Equilibrium—The Stable State

A pivotal point in the book, Chapter 12 has two principal aims: First, to establish the equilibrium state as the likely outcome of most chemical processes, with an eye also toward its eventual thermodynamic and statistical rationalization. Second, to provide abundant practice in manipulating the equilibrium constant and reaction quotient. The exercises support both aims.

We begin with an extended series of questions dealing with the nature of equilibrium (Sections 12-1 through 12-3) and the law of mass action (Sections 12-4 through 12-6).

1. We say that a reaction goes to completion if at least one of the reactants is entirely converted into products—as happens to the limiting reactant when the equilibrium constant is very large. A reaction may also be driven to completion by continuous removal of products during the process.
2. A reaction effectively “ends” as soon as it reaches a state of dynamic equilibrium, whereby reactants are converted into products at the same rate that products are reconverted back into reactants. Equilibrium takes hold when the concentrations of reactants and products conform to the ratio set by the mass-action expression, after which there is no longer a spontaneous drive to form product at the expense of reactant. Microscopically, the opposing processes continue to run in perpetual stalemate. Macroscopically, nothing in the system appears to change.
3. Chemical equilibrium is *dynamic* because two opposing processes proceed at the same rate: a forward reaction, in which reactants become products; and a reverse reaction, in which these same products are transformed back into the original reactants. The equilibrium thus attained remains subject to external manipulation, however, and a seemingly “dead” reaction can be restarted in any number of ways, including addition of reactants, removal of products, change of temperature, change of pressure, and so forth. Moreover, no chemical system ever reaches a global minimum below which there is potentially no state of still greater stability. No equilibrium is truly final.

4. No. Given just the numerical value of $K(T)$ and the stoichiometry of a reaction, we cannot determine the equilibrium concentrations. We need the initial concentrations in order to construct an equation that will fix the composition at equilibrium. The value of $K(T)$ tells us only whether the mass-action ratio will tend toward products ($K \gg 1$) or toward reactants ($K \ll 1$) when the process is complete.

5. No, there is no unique combination of $[A]_{\text{eq}}$, $[B]_{\text{eq}}$, $[C]_{\text{eq}}$, and $[D]_{\text{eq}}$ that will satisfy the constraints imposed by $K(T)$ to the exclusion of all other possibilities. The same mass-action ratio—the same numerical value of $K(T)$ —can be realized in an infinite number of ways by choosing different values for each of the four equilibrium concentrations.

Note that a similar flexibility is granted to an ideal gas, which can satisfy the equation $PV = nRT$ with an infinite number of combinations of P , V , n , and T .

6. The temperature dependence is implicit in the number $K(T)$: a combination of *all* the concentrations at equilibrium, expressed as the mass-action ratio. The distribution of products and reactants is different at different temperatures, and the variation is captured by the changing value of $K(T)$.

An endothermic reaction, for example, will yield proportionately more products at a higher temperature. The mass-action ratio increases as T increases, and $K(T)$ increases along with it.

7. The equilibrium constant is a function of temperature alone. Its numerical value is unaffected by changes in pressure or concentration. See Sections 12-5 and 12-6 of *PoC*, together with Examples 12-11 through 12-15.

(a) No. Changing the concentrations of reactants and products may shift the *position* of equilibrium, but such action does not change the equilibrium constant itself. Although there may be more or less of a given species at equilibrium, the mass-action ratio—which is established by all the concentrations together—remains unaltered.

(b) No, for the same reasons as in (a). Changing the volume of the system (typically where gases are involved) is tantamount to changing the pressure or concentration of each species. The numerical value of K stays the same.

(c) No. A change in pressure will not change the equilibrium constant itself, as already noted under (b).

(d) Yes, the equilibrium constant depends on temperature. The numerical value of $K(T)$ varies with T .

(e) No. A catalyst affects the rate at which a reaction comes to equilibrium but not the eventual distribution of products and reactants. $K(T)$ stays the same whether or not a catalyst facilitates the process. See Sections 3-6 and 18-5.

8. We consider possible shifts in equilibrium for the following hypothetical reaction:



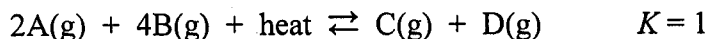
(a) Since the process is exothermic, a rise in temperature has the effect of adding more “product”: heat. The system dissipates this stress by shifting to the reverse reaction (which is endothermic), thereby consuming the additional heat as products turn back into reactants. The increase in temperature lowers the magnitude of $K(T)$ as well, ensuring a smaller proportion of products C and D when the system comes to its new equilibrium at a value $K < 1$.

(b) A drop in temperature produces the opposite effect. The equilibrium constant for an exothermic reaction grows larger at lower temperatures, favoring a greater proportion of products once equilibrium is restored. Interpreted as a stress, a lower temperature serves to remove heat from the system and thereby pull the reaction to the right: toward the formation of additional products. The value of K will be greater than 1 when equilibrium is reestablished.

(c) Six moles of gaseous reactants ($2A + 4B$) combine to form two moles of gaseous products ($C + D$). The system alleviates any increased pressure by moving to the right, effectively reducing the total number of species from six to two. More products are formed, but the numerical value of $K(T)$ stays fixed at 1.

(d) Conversely, a decrease in pressure drives the reaction to the left. The lower pressure instantly raises the reaction quotient, Q , above the level of K , leaving the system temporarily with too many products and too few reactants. Reactants are regenerated at the expense of products, again with no change in the value of $K(T)$.

9. The reaction



has the same stoichiometry as in Exercise 8, but now the process is endothermic in the forward direction. Changes caused by shifts in temperature will be opposite to those predicted for the exothermic reaction, but changes caused by shifts in pressure will be exactly the same.

(a) Heat, registered as a change in temperature, functions as a reactant in an endothermic process. An increase in temperature thus will shift the equilibrium toward the right, favoring a greater proportion of products while dissipating the stress of additional heat. The new value of $K(T)$ will be greater than 1. See pages 450–452, 456–457, and Example 12-15 in *PoC*.

(b) Opposite to (a): A lower temperature, equivalent to the removal of a reactant (heat), favors the regeneration of reactants. The new value of $K(T)$ will be less than 1.

(c) Compare the present endothermic process with the otherwise identical exothermic process put forth in Exercise 8(c). Our conclusions are the same for both: Six moles of gaseous reactants ($2A + 4B$) combine to form two moles of gaseous products ($C + D$). The system alleviates any increased pressure by moving in the direction of fewer particles—to the right, so as to replace six species by only two. More products are formed, but the equilibrium constant stays fixed at $K(T) = 1$. Pressure has no effect on the numerical value of $K(T)$.

An increase in pressure thus drives the reaction to the right, for precisely the same reasons it would do so even if the process were exothermic. The absorption or evolution of heat is irrelevant. See pages 452–455 in *PoC*, as well as Examples 12-13 and 12-14 (beginning on page R12.20).

(d) Opposite to (c): A decrease in pressure drives the reaction to the left, toward reactants. The lower pressure instantly elevates the reaction quotient

$$Q = \frac{P_C P_D}{P_A^2 P_B^4}$$

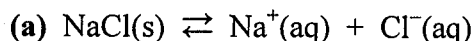
to a value greater than K , leaving the system temporarily with too many products and too few reactants. Products are consumed and reactants are formed, but the partial pressures at the new equilibrium yield the same mass-action ratio as before: $K(T) = 1$.

10. A catalyst lowers the activation energy of a reaction, speeding up both the forward and reverse reactions in equal measure. Although the reaction comes to equilibrium more quickly, the final proportions of products and reactants remain the same. Neither the algebraic form nor the numerical value of $K(T)$ is altered by the action of a catalyst. See Sections 3-6 and 18-5.

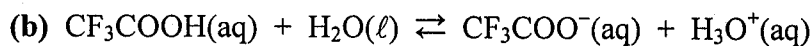
11. No. Even if we know the concentration of each species at equilibrium, we cannot reconstruct the initial conditions. The same final concentrations may be reached from different starting points, and the state of equilibrium gives us no information about any prior history of the system. We know only the present, unchanging, macroscopic endpoint—not the path taken to reach it. See Section 12-1.

12. The equilibrium constant, $K(T)$, is a fixed number at a given temperature: a target value for the mass-action ratio. Concentrations of all products and reactants at equilibrium must conform to the specific number set by $K(T)$. By contrast, the variable reaction quotient, Q , provides an instantaneous measure of the mass-action ratio at any point during the reaction—typically not at equilibrium. The reaction quotient can take any value at all, either greater than K or less than K , except when the system finally attains equilibrium. At equilibrium, Q becomes equal to K . See Section 12-4 and Example 12-8.

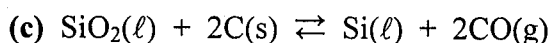
13. A *homogeneous* equilibrium takes place in just one phase. A *heterogeneous* equilibrium involves two or more different phases.



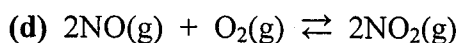
Heterogeneous: NaCl(s) exists in a solid phase, but $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ exist in an aqueous phase (a solution).



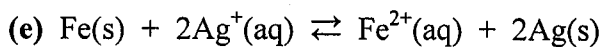
Homogeneous: The reaction takes place entirely in a common *solution* phase, which includes liquid water.



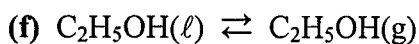
Heterogeneous: $\text{SiO}_2(\ell)$ and $\text{Si}(\ell)$ are liquids; C(s) is a solid; CO(g) is a gas.



Homogeneous: Reactants and products are all in the gas phase.

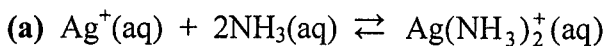


Heterogeneous: Fe(s) and Ag(s) are solids; $\text{Ag}^+(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$ are ions in aqueous solution.

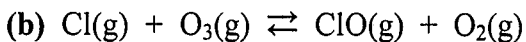


Heterogeneous: The equation describes a phase equilibrium between liquid ethanol and its vapor.

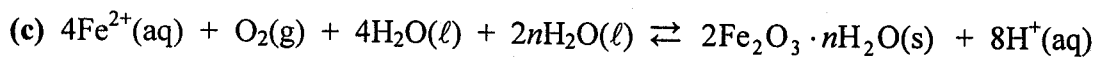
14. Similar to the preceding exercise.



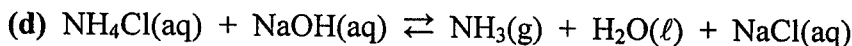
Homogeneous: The reaction takes place entirely in aqueous solution.



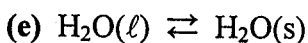
Homogeneous: The reaction takes place entirely in the gas phase.



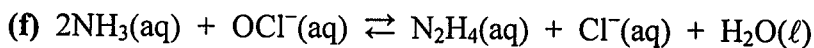
Heterogeneous: Some species exist in an aqueous or liquid phase, whereas others are either solids or gases.



Heterogeneous: Ammonia (NH_3) is a gas, but the other species all react in a common aqueous phase.



Heterogeneous: The equation describes a phase equilibrium between liquid and solid water.

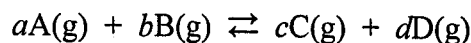


Homogeneous: The reaction takes place entirely in aqueous solution.

15. Define the equilibrium constants K_c and K_p as

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

for the prototypical gas-phase reaction



Then substitute the ideal-gas concentrations

$$[\text{X}] = \frac{n_X}{V} = \frac{P_X}{RT}$$

to express K_c in terms of K_p :

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^c \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b} = \frac{P_C^c P_D^d}{P_A^a P_B^b} (RT)^{a+b-c-d} = K_p (RT)^{a+b-c-d}$$

To convert between K_c and K_p , we shall need to calculate the factor RT —or, strictly

speaking, the dimensionless factor $c^\circ RT/P^\circ$, which introduces unit reference values of $c^\circ = 1 \text{ mol L}^{-1}$ and $P^\circ = 1 \text{ atm}$. At 873 K (600°C), the specific number to be used is 71.6:

$$\frac{c^\circ RT}{P^\circ} = \frac{(1 \text{ mol L}^{-1})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(873 \text{ K})}{1 \text{ atm}} = 71.6$$

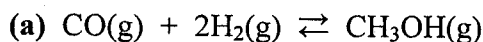
Putting everything together, finally, we have the general relationship

$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n}$$

where Δn is the change in moles of gas:

$$\Delta n = \text{no. moles of gaseous products} - \text{no. moles of gaseous reactants}$$

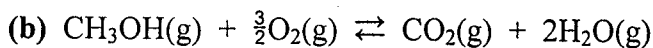
See pages 446, 449, and 460 in *PoC*, together with Example 12-4 (beginning on page R12.9).



$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \quad K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} P_{\text{H}_2}^2}$$

$$\Delta n = 1 - (1 + 2) = -2$$

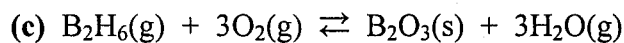
$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = (71.6)^2 = 5.13 \times 10^3$$



$$K_c = \frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_3\text{OH}][\text{O}_2]^{3/2}} \quad K_p = \frac{P_{\text{CO}_2} P_{\text{H}_2\text{O}}^2}{P_{\text{CH}_3\text{OH}} P_{\text{O}_2}^{3/2}}$$

$$\Delta n = (1 + 2) - \left(1 + \frac{3}{2} \right) = \frac{1}{2}$$

$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = (71.6)^{-1/2} = 0.118$$

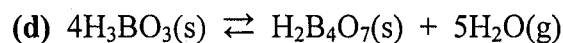


$$K_c = \frac{[\text{H}_2\text{O}]^3}{[\text{B}_2\text{H}_6][\text{O}_2]^3} \quad K_p = \frac{P_{\text{H}_2\text{O}}^3}{P_{\text{B}_2\text{H}_6} P_{\text{O}_2}^3}$$

$$\Delta n = 3 - (1 + 3) = -1$$

$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = (71.6)^1 = 71.6$$

The solid product, $\text{B}_2\text{O}_3(\text{s})$, does not appear in the equilibrium constant.



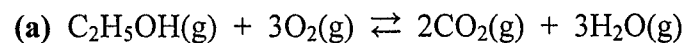
$$K_c = [\text{H}_2\text{O}]^5 \quad K_p = P_{\text{H}_2\text{O}}^5$$

$$\Delta n = 5 - 0 = 5$$

$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = (71.64)^{-5} = 5.30 \times 10^{-10}$$

Only the gaseous species, $\text{H}_2\text{O}(\text{g})$, appears in the equilibrium constant.

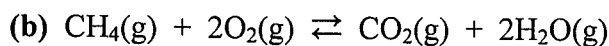
16. Use the same method as in the preceding exercise.



$$K_c = \frac{[\text{CO}_2]^2 [\text{H}_2\text{O}]^3}{[\text{C}_2\text{H}_5\text{OH}] [\text{O}_2]^3} \quad K_p = \frac{P_{\text{CO}_2}^2 P_{\text{H}_2\text{O}}^3}{P_{\text{C}_2\text{H}_5\text{OH}} P_{\text{O}_2}^3}$$

$$\Delta n = (2 + 3) - (1 + 3) = 1$$

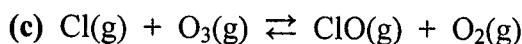
$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = (71.6)^{-1} = 1.40 \times 10^{-2}$$



$$K_c = \frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_4][\text{O}_2]^2} \quad K_p = \frac{P_{\text{CO}_2} P_{\text{H}_2\text{O}}^2}{P_{\text{CH}_4} P_{\text{O}_2}^2}$$

$$\Delta n = (1+2) - (1+2) = 0$$

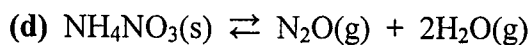
$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = \left(\frac{c^\circ RT}{P^\circ} \right)^0 = 1$$



$$K_c = \frac{[\text{ClO}][\text{O}_2]}{[\text{Cl}][\text{O}_3]} \quad K_p = \frac{P_{\text{ClO}} P_{\text{O}_2}}{P_{\text{Cl}} P_{\text{O}_3}}$$

$$\Delta n = (1+1) - (1+1) = 0$$

$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = \left(\frac{c^\circ RT}{P^\circ} \right)^0 = 1$$



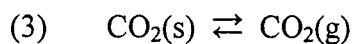
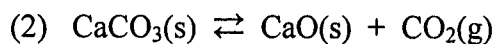
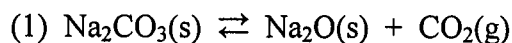
$$K_c = [\text{N}_2\text{O}][\text{H}_2\text{O}]^2 \quad K_p = P_{\text{N}_2\text{O}} P_{\text{H}_2\text{O}}^2$$

$$\Delta n = (1+2) - 0 = 3$$

$$\frac{K_c}{K_p} = \left(\frac{c^\circ RT}{P^\circ} \right)^{-\Delta n} = (71.6)^{-3} = 2.72 \times 10^{-6}$$

The solid reactant, $\text{NH}_4\text{NO}_3(\text{s})$, does not appear in the equilibrium constant.

17. The three reactions



do share the same algebraic expression for K_p :

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

Each equilibrium is chemically different, however, and each equilibrium constant has a different numerical value.

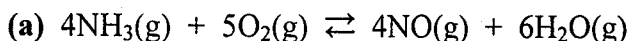
Equation (1) describes a heterogeneous equilibrium involving gaseous CO_2 , solid Na_2O , and solid Na_2CO_3 . When the reaction comes to equilibrium, all three species will be present simultaneously and then—and only then—will the partial pressure of CO_2 in *this* particular chemical environment have a certain fixed numerical value.

Similarly, equation (2) describes a heterogeneous equilibrium involving gaseous CO_2 and two other species in a solid phase: CaO and CaCO_3 . At equilibrium, with these three particular components present, the partial pressure of CO_2 will again be fixed—but the equilibrium pressure will differ from its numerical value in reaction (1).

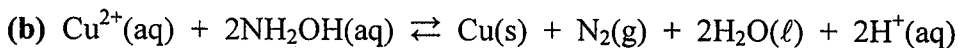
Finally, the equilibrium pressure of CO_2 will take on yet another value when gaseous and solid CO_2 coexist in the phase equilibrium described by equation (3).

Thus the form of the equilibrium expression is the same, but its numerical value is different for each system. Each equilibrium requires its own particular reactants and products.

18. For gaseous equilibria, the equilibrium constant is properly expressed in terms of pressure.



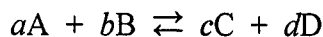
$$K = \frac{P_{\text{NO}}^4 P_{\text{H}_2\text{O}}^6}{P_{\text{NH}_3}^4 P_{\text{O}_2}^5}$$



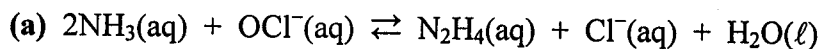
$$K = \frac{P_{\text{N}_2} [\text{H}^+]^2}{[\text{Cu}^{2+}] [\text{NH}_2\text{OH}]^2}$$

Neither $\text{H}_2\text{O}(\ell)$ nor $\text{Cu}(\text{s})$ appears in the expression above for K . The concentrations of pure liquids and solids hold constant, and their fixed values are implicit in the numerical value of K .

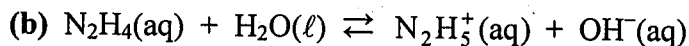
19. Pure liquids and pure solids do not appear in the equilibrium constant K_c :



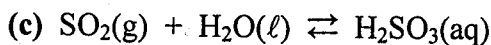
$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$



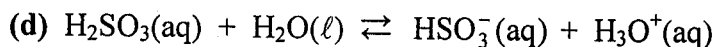
$$K_c = \frac{[\text{N}_2\text{H}_4][\text{Cl}^-]}{[\text{NH}_3]^2[\text{OCI}^-]}$$



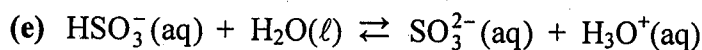
$$K_c = \frac{[\text{N}_2\text{H}_5^+][\text{OH}^-]}{[\text{N}_2\text{H}_4]}$$



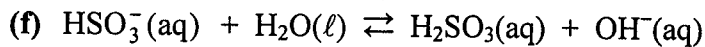
$$K_c = \frac{[\text{H}_2\text{SO}_3]}{[\text{SO}_2]}$$



$$K_c = \frac{[\text{HSO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{SO}_3]}$$

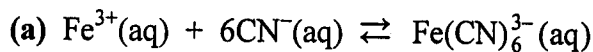


$$K_c = \frac{[\text{SO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_3^-]}$$

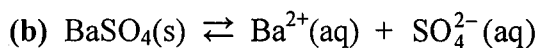


$$K_c = \frac{[\text{H}_2\text{SO}_3][\text{OH}^-]}{[\text{HSO}_3^-]}$$

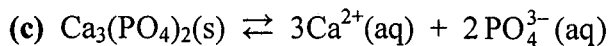
20. More of the same.



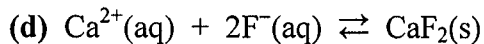
$$K_c = \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}^{3+}][\text{CN}^-]^6}$$



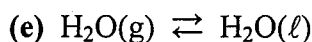
$$K_c = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$



$$K_c = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

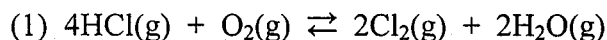


$$K_c = \frac{1}{[\text{Ca}^{2+}][\text{F}^-]^2}$$

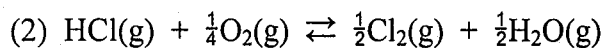


$$K_c = \frac{1}{[\text{H}_2\text{O}(g)]}$$

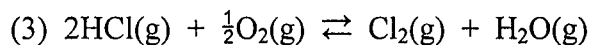
21. The equations differ only by an overall multiplicative constant:



$$K_1 = \frac{P_{\text{Cl}_2}^2 P_{\text{H}_2\text{O}}^2}{P_{\text{HCl}}^4 P_{\text{O}_2}} = 13.3 \text{ at } 753 \text{ K (given)}$$



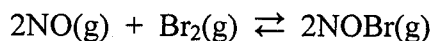
$$K_2 = \frac{P_{\text{Cl}_2}^{1/2} P_{\text{H}_2\text{O}}^{1/2}}{P_{\text{HCl}} P_{\text{O}_2}^{1/4}} = \left(\frac{P_{\text{Cl}_2}^2 P_{\text{H}_2\text{O}}^2}{P_{\text{HCl}}^4 P_{\text{O}_2}} \right)^{1/4} = (K_1)^{1/4} = 13.3^{1/4} = 1.91$$



$$K_3 = \frac{P_{\text{Cl}_2} P_{\text{H}_2\text{O}}}{P_{\text{HCl}}^2 P_{\text{O}_2}^{1/2}} = \left(\frac{P_{\text{Cl}_2}^2 P_{\text{H}_2\text{O}}^2}{P_{\text{HCl}}^4 P_{\text{O}_2}} \right)^{1/2} = (K_1)^{1/2} = 13.3^{1/2} = 3.65$$

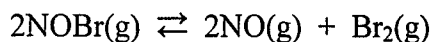
There is no inconsistency provided that we associate the correct numerical value of K with the corresponding stoichiometric equation used to define it. The proportions of reactants and products at equilibrium are unaffected by the particular choice of chemical equation. See also Example 12-5, beginning on page R12.11 of *PoC*.

22. Similar to Example 12-3. Start with the reaction written in the forward direction:



$$K_p = \frac{P_{\text{NOBr}}^2}{P_{\text{NO}}^2 P_{\text{Br}_2}} = 2.40 \text{ at } 100^\circ\text{C} \quad (\text{given})$$

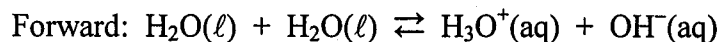
The equilibrium constant for the reverse reaction, K'_p , is the reciprocal of K_p for the forward reaction:



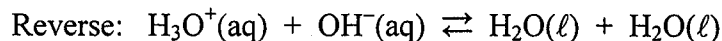
$$K'_p = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2} = \frac{1}{K_p} = \frac{1}{2.40} = 0.417$$

Exercises 23 through 35 serve mostly as an introduction to acid–base equilibria, the subject of Chapter 16.

23. The equilibrium constants for forward and reverse processes are reciprocals, as demonstrated on page 452 of *PoC* and also in Example 12-3. Remember again that $[\text{H}_2\text{O}(\ell)]$, a fixed number, is omitted from K :

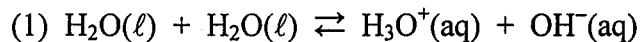


$$K = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad (\text{given})$$

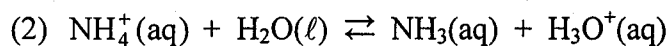


$$K' = \frac{1}{[\text{H}_3\text{O}^+][\text{OH}^-]} = \frac{1}{K} = \frac{1}{1.0 \times 10^{-14}} = 1.0 \times 10^{14}$$

24. First, write mass-action expressions for (1) and (2):

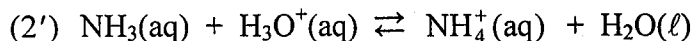


$$K_1 = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$



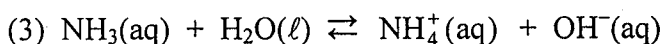
$$K_2 = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = 5.7 \times 10^{-10}$$

Second, compute K for reaction (2) run in the opposite direction:



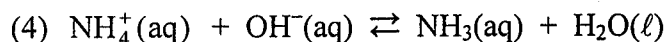
$$K'_2 = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}_3\text{O}^+]} = \frac{1}{K_2} = \frac{1}{5.7 \times 10^{-10}}$$

Third, observe that reaction (3) is the sum of reactions (1) and (2'). The equilibrium constant K_3 is the product of K_1 and K'_2 :



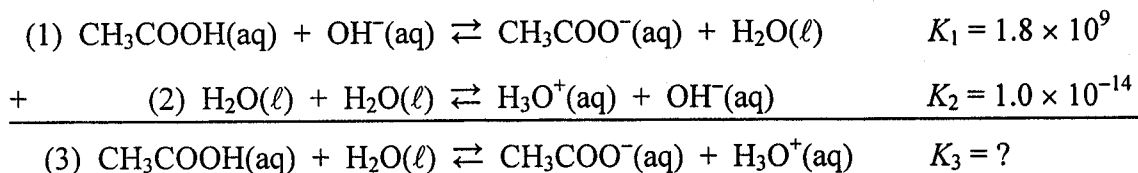
$$\begin{aligned} K_3 &= \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-] \times \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}_3\text{O}^+]} = K_1 K'_2 \\ &= (1.0 \times 10^{-14}) \left(\frac{1}{5.7 \times 10^{-10}} \right) = 1.75 \times 10^{-5} \\ &= 1.8 \times 10^{-5} \quad (2 \text{ sig fig}) \end{aligned}$$

Finally, reaction (4) is the reverse of reaction (3). The two equilibrium constants are reciprocals:



$$K_4 = \frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]} = \frac{1}{K_3} = \frac{1}{1.75 \times 10^{-5}} = 5.7 \times 10^4$$

25. Recognize that reaction (3) is the sum of reactions (1) and (2):

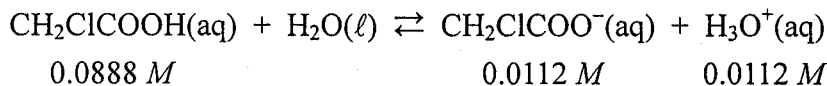


The net equilibrium constant, K_3 , is therefore the product of K_1 and K_2 :

$$\begin{aligned}
 K_3 &= \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{OH}^-]} \times [\text{H}_3\text{O}^+][\text{OH}^-] = K_1 K_2 \\
 &= (1.8 \times 10^9)(1.0 \times 10^{-14}) \\
 &= 1.8 \times 10^{-5}
 \end{aligned}$$

See also Example 12-6 in *PoC*, beginning on page R12.12.

26. Knowing both the reaction stoichiometry and the equilibrium concentrations of all species,

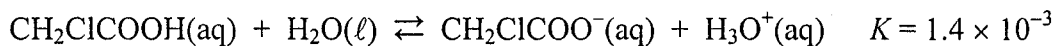


we can evaluate the equilibrium constant at 25°C:

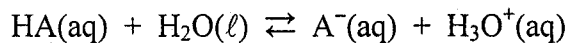
$$K = \frac{[\text{CH}_2\text{ClCOO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_2\text{ClCOOH}]} = \frac{(0.0112)(0.0112)}{0.0888} = 1.41 \times 10^{-3}$$

See also Example 12-2 in *PoC*, beginning on page R12.7.

27. From the two previous exercises we know the equilibrium constants for acetic acid and chloroacetic acid at 25°C:



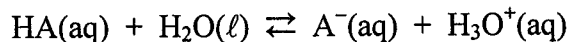
Each equation describes the dissociation of an acid (HA) into an anion (A⁻) and hydronium ion (H₃O⁺):



$$K = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

The acid with the larger dissociation constant produces the greater concentration of hydronium ions at equilibrium. Chloroacetic acid, CH₂ClCOOH, is therefore stronger than acetic acid.

28. The general reaction and equilibrium expression are described in the solution to Exercise 27:



$$K = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

For benzoic acid at 25°C, we have $K = 6.5 \times 10^{-5}$:

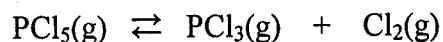
$$K = \frac{[\text{C}_7\text{H}_5\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_7\text{H}_5\text{O}_2]} = \frac{(3.6 \times 10^{-3})(3.6 \times 10^{-3})}{(2.0 \times 10^{-1})} = 6.5 \times 10^{-5}$$

The corresponding value for formic acid is 1.80×10^{-4} :

$$K = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]} = \frac{(2.24 \times 10^{-3})(2.24 \times 10^{-3})}{(2.78 \times 10^{-2})} = 1.80 \times 10^{-4}$$

Formic acid is stronger than benzoic acid. HCOOH yields a greater concentration of hydronium ions at equilibrium.

29. Introduced into a volume of 1.00 L, each component (1.00 mol) has an initial concentration of 1.00 mol L^{-1} in the gas-phase reaction under consideration:



Initial: 1.00 M 1.00 M 1.00 M

We also know that the reaction proceeds in the forward direction, since the concentration of Cl_2 eventually grows from its starting value of 1.00 M to its equilibrium value of 1.20 M.

(a) Given the stoichiometry and initial conditions, we can write symbolic expressions for the concentrations at equilibrium:

	INITIAL		CHANGE		EQUILIBRIUM
$[\text{PCl}_5]$	= 1.00	-	x	=	$1.00 - x$
$[\text{PCl}_3]$	= 1.00	+	x	=	$1.00 + x$
$[\text{Cl}_2]$	= 1.00	+	x	=	$1.00 + x$

We are told, moreover, that the equilibrium concentration of Cl_2 is 1.20 M :

	INITIAL		CHANGE		EQUILIBRIUM
$[\text{Cl}_2]$	= 1.00	+	x	=	1.20

From that, we obtain $x = 0.20 M$ and thereby determine the final concentrations of all species:

$$[\text{PCl}_5] = 1.00 M - x = 0.80 M$$

$$[\text{PCl}_3] = 1.00 M + x = 1.20 M$$

$$[\text{Cl}_2] = 1.00 M + x = 1.20 M$$

(b) The equilibrium constant K_c follows directly from the equilibrium concentrations:

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(1.20)(1.20)}{0.80} = 1.8 \quad (T = 523 \text{ K})$$

(c) The relationship between K_p and K_c ,

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{\Delta n}$$

is discussed on page 460 of *PoC*, as well as in Example 12-4 (beginning on page R12.9). Recall that the reference values c° and P° are 1 mol L^{-1} and 1 atm, respectively, and that the symbol Δn denotes the net change in moles of gas:

$$\Delta n = \text{no. moles of gaseous products} - \text{no. moles of gaseous reactants}$$

See also the solution to Exercise 15.

Given $\Delta n = 1$ for our reaction,



$$\Delta n = (1 + 1) - 1 = 1$$

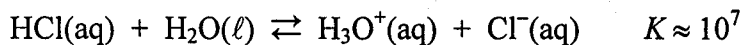
we see at once that

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)$$

and we establish a numerical value at $T = 523 \text{ K}$:

$$K_p = 1.8 \times \frac{(1 \text{ mol L}^{-1})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(523 \text{ K})}{1 \text{ atm}} = 77$$

30. The exceedingly large equilibrium constant for the reaction



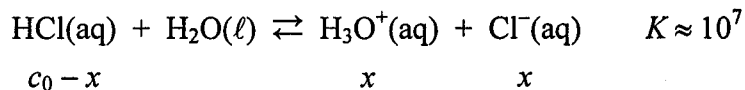
suggests that HCl is a strong acid, which we expect to dissociate completely in solution:

	INITIAL		CHANGE		EQUILIBRIUM
[HCl]	= c_0	-	c_0	≈	0
[H ₃ O ⁺]	= 0	+	c_0	≈	c_0
[Cl ⁻]	= 0	+	c_0	≈	c_0

If so, then we can determine the equilibrium concentrations of all species simply from the initial concentration of the acid, c_0 .

The detailed calculations below show that this assumption is indeed justified, and henceforth we shall avoid explicit numerical solution of the mass-action expression for a strong acid.

(a) Given an initial concentration of HCl, c_0 , let us assume that some concentration x dissociates into H₃O⁺ and Cl⁻. The resulting equilibrium concentrations are expressed symbolically as follows:



Writing the mass-action expression,

$$K = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]} = \frac{x^2}{c_0 - x}$$

we obtain a quadratic equation for x :

$$x^2 = K(c_0 - x)$$

$$0 = x^2 + Kx - Kc_0$$

Note that this equation matches the general form

$$ax^2 + bx + c = 0$$

with

$$a = 1 \quad b = K \quad c = -Kc_0$$

Its two solutions are given by the quadratic formula (see Section B-3 of *PoC*):

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K \pm \sqrt{K^2 + 4Kc_0}}{2}$$

Substituting for K and c_0 ,

$$K = 10^7$$

$$c_0 = \frac{1.00 \text{ mol}}{0.10 \text{ L}} = 10. \text{ M}$$

we then use the binomial approximation

$$\sqrt{1 + \varepsilon} = (1 + \varepsilon)^{1/2} \approx 1 + \frac{\varepsilon}{2} \quad (\varepsilon \ll 1)$$

to evaluate the quadratic formula for x :

$$\begin{aligned} x &= \frac{-10^7 \pm \sqrt{(10^7)^2 + 4(10^7)(10)}}{2} \\ &= \frac{-10^7 \pm \sqrt{10^{14}(1 + 4 \times 10^{-6})}}{2} = \frac{-10^7 \pm 10^7 \sqrt{1 + 4 \times 10^{-6}}}{2} \\ &\approx \frac{-10^7 \pm 10^7(1 + 2 \times 10^{-6})}{2} = \frac{-10^7 \pm 10^7 \pm 20}{2} = 10, -10^7 \end{aligned}$$

Of the two solutions, we reject $x_- \approx -10^7$ as unphysical and conclude that virtually all of the HCl is dissociated into H_3O^+ and Cl^- at equilibrium:

$$x_+ \approx 10. \text{ M}$$

(b) Given an initial concentration of

$$c_0 = \frac{1.00 \text{ mol}}{1.00 \text{ L}} = 1.00 \text{ M}$$

we solve the quadratic equation that results:

$$0 = x^2 + Kx - Kc_0$$

$$x = \frac{-10^7 \pm \sqrt{10^{14} + (4 \times 10^7)}}{2} \approx 1, -10^7$$

The physically valid solution

$$x_+ \approx 1.00 \text{ M}$$

again indicates that effectively 100% of the acid is dissociated in solution.

(c) A similar calculation for an initial concentration

$$c_0 = \frac{1.00 \text{ mol}}{10.00 \text{ L}} = 0.100 \text{ M}$$

yields a similar result:

$$x \approx 0.100 \text{ M} = c_0$$

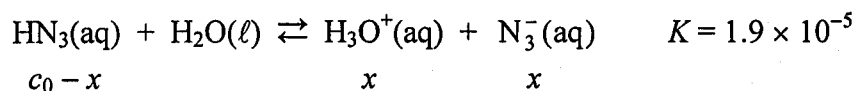
31. As explained in Exercise 30, we assume that one mole of HCl produces one mole of $\text{H}_3\text{O}^+(\text{aq})$ and one mole of $\text{Cl}^-(\text{aq})$ regardless of the total volume.

(a) $\approx 1.00 \text{ mol } \text{H}_3\text{O}^+(\text{aq})$ and $1.00 \text{ mol } \text{Cl}^-(\text{aq})$ in 0.10 L

(b) $\approx 1.00 \text{ mol } \text{H}_3\text{O}^+(\text{aq})$ and $1.00 \text{ mol } \text{Cl}^-(\text{aq})$ in 1.00 L

(c) $\approx 1.00 \text{ mol } \text{H}_3\text{O}^+(\text{aq})$ and $1.00 \text{ mol } \text{Cl}^-(\text{aq})$ in 10.00 L

32. We first set up the problem in general form,



with equilibrium concentrations represented as follows:

		INITIAL		CHANGE		EQUILIBRIUM
$[\text{HN}_3]$	=	c_0	-	x	=	$c_0 - x$
$[\text{H}_3\text{O}^+]$	=	0	+	x	=	x
$[\text{N}_3^-]$	=	0	+	x	=	x

Next, we put together the mass-action expression and prepare to solve for x :

$$K = \frac{[\text{H}_3\text{O}^+][\text{N}_3^-]}{[\text{HN}_3]} = \frac{x^2}{c_0 - x} = 1.9 \times 10^{-5}$$

(a) The initial concentration of HN_3 is

$$c_0 = \frac{1.00 \text{ mol}}{0.10 \text{ L}} = 10. \text{ M}$$

and the resulting expression is nominally a full quadratic equation ($ax^2 + bx + c = 0$):

$$K = \frac{x^2}{10 - x} = 1.9 \times 10^{-5}$$

Since K is only about 10^{-5} , however, we expect x to be much smaller than 10. Our usual approximation (see Example 12-10 in *PoC*) is then to take

$$10 - x \approx 10$$

and rewrite the equation as a simple square root:

$$\frac{x^2}{10} \approx 1.9 \times 10^{-5}$$

$$x^2 \approx 1.9 \times 10^{-4}$$

$$x \approx 1.4 \times 10^{-2}$$

Concentrations at equilibrium are given below:

$$[\text{HN}_3] = c_0 - x = (10. - 0.014) \text{ M} \approx 10. \text{ M}$$

$$[\text{H}_3\text{O}^+] = x = 0.014 \text{ M}$$

$$[\text{N}_3^-] = x = 0.014 \text{ M}$$

Note that the approximation proves justified to two significant figures: $0.014 \ll 10$.

(b) An initial concentration of

$$c_0 = \frac{1.00 \text{ mol}}{1.00 \text{ L}} = 1.00 \text{ M}$$

gives us the following equation to solve:

$$\frac{x^2}{1.00 - x} = 1.9 \times 10^{-5}$$

Taking $x \ll 1$, we obtain an approximate but sufficiently accurate result:

$$x^2 \approx 1.9 \times 10^{-5}$$

$$x \approx 4.4 \times 10^{-3}$$

At equilibrium:

$$[\text{HN}_3] = c_0 - x = (1.00 - 0.0044) \text{ M} \approx 1.00 \text{ M}$$

$$[\text{H}_3\text{O}^+] = x = 0.0044 \text{ M}$$

$$[\text{N}_3^-] = x = 0.0044 \text{ M}$$

(c) The procedure for the third initial concentration,

$$c_0 = \frac{1.00 \text{ mol}}{10.00 \text{ L}} = 0.100 \text{ M}$$

is the same as for the first two:

$$\frac{x^2}{0.100 - x} = 1.9 \times 10^{-5}$$

$$\frac{x^2}{0.100} \approx 1.9 \times 10^{-5}$$

$$x^2 \approx 1.9 \times 10^{-6}$$

$$x \approx 1.4 \times 10^{-3}$$

At equilibrium:

$$[\text{HN}_3] = c_0 - x = (0.100 - 0.0014) \text{ M} = 0.099 \text{ M}$$

$$[\text{H}_3\text{O}^+] = x = 0.0014 \text{ M}$$

$$[\text{N}_3^-] = x = 0.0014 \text{ M}$$

33. Take the system described in part (a) as a representative example. From the preceding exercise, we know that

$$[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{N}_3^-]_{\text{eq}} = 0.014 \text{ M}$$

when 1.00 mol HN_3 is dissolved in 0.10 L at 25°C. To calculate the corresponding amount of either H_3O^+ or N_3^- , in moles, we simply multiply this equilibrium concentration by the volume:

$$\frac{0.014 \text{ mol}}{\text{L}} \times 0.10 \text{ L} = 0.0014 \text{ mol} \quad (\text{H}_3\text{O}^+ \text{ or } \text{N}_3^-)$$

The remaining calculations are done in the same way:

	$[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{N}_3^-]_{\text{eq}} \text{ (M)}$	VOLUME (L)	MOLES
(a)	0.014	0.10	0.0014
(b)	0.0044	1.00	0.0044
(c)	0.0014	10.00	0.014

34. The contrasting results bring out the difference between a strong acid and a weak acid. The strong acid, HCl, ionizes completely regardless of volume and initial concentration (Exercises 30 and 31). For the weak acid, however, the extent of ionization is determined by the initial concentration of the undissociated form (Exercises 32 and 33).

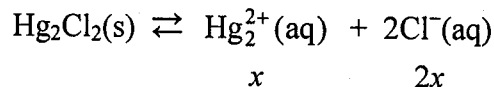
Acid–base equilibria are treated comprehensively in Chapter 16.

35. Various factors determine the strength of an acid (HA). For example, electron-withdrawing groups (such as Cl) sometimes produce a strongly polarized A–H bond, readily broken to yield H^+ and A^- . Weak, highly polarized A–H bonds therefore contribute favorably to the strength of an acid. Other considerations include the size and charge distribution of the detached anion, A^- . Anions that can disperse the negative charge over a comparatively large volume gain a measure of stability. The more stable the anion, the stronger the acid. See Chapter 16.

Exercises 36 and 37 deal with the dissolution and precipitation of inorganic salts, an area to be explored thoroughly in Chapter 15.

36. Consider the heterogeneous equilibrium involving mercurous chloride in its

solid and dissolved forms. One mole of mercury(I) ions and two moles of chloride ions are produced per mole of compound dissolved:



	INITIAL		CHANGE		EQUILIBRIUM
$[\text{Hg}_2^{2+}]$	= 0	+	x	=	x
$[\text{Cl}^-]$	= 0	+	$2x$	=	$2x$

Setting up the equilibrium expression,

$$K = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = x(2x)^2 = 4x^3 = 1.5 \times 10^{-18}$$

we obtain the unknown concentration x as the cube root of $\frac{1}{4}K$:

$$4x^3 = 1.5 \times 10^{-18}$$

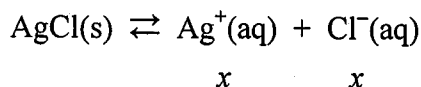
$$x = 7.2 \times 10^{-7}$$

Note that the solid is omitted from the equilibrium expression. The resulting equilibrium concentrations are given below:

$$[\text{Hg}_2^{2+}] = x = 7.2 \times 10^{-7} \text{ M}$$

$$[\text{Cl}^-] = 2x = 1.4 \times 10^{-6} \text{ M}$$

37. Similar. Here we have the dissolution-precipitation of silver chloride



and its associated equilibrium constant:

$$K = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.34 \times 10^{-5} = 1.3 \times 10^{-5} \quad (2 \text{ sig fig})$$

The equilibrium concentrations (expressed as moles per liter) are fixed,

$$x = [\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ M}$$

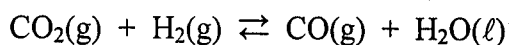
but the actual number of moles depends on the volume of solution.

$$(a) \frac{1.3 \times 10^{-5} \text{ mol}}{\text{L}} \times 1.00 \text{ L} = 1.3 \times 10^{-5} \text{ mol}$$

$$(b) \frac{1.3 \times 10^{-5} \text{ mol}}{\text{L}} \times (1.00 \times 10^{-3} \text{ L}) = 1.3 \times 10^{-8} \text{ mol}$$

$$(c) \frac{1.3 \times 10^{-5} \text{ mol}}{\text{L}} \times (1.00 \times 10^3 \text{ L}) = 1.3 \times 10^{-2} \text{ mol}$$

38. In this exercise and the next, we consider the production of carbon monoxide and water from carbon dioxide and hydrogen:



$$K_p = \frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} = 3.2 \times 10^{-4} \quad (25^\circ \text{C})$$

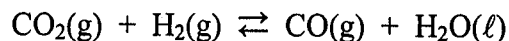
Note that liquid water does not appear in the equilibrium expression.

(a) We use the specified pressures to show that the reaction quotient has the nonequilibrium value 1.00:

$$Q = \frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} = \frac{1.00}{(1.00)(1.00)} = 1.00 > K_p$$

Since Q is greater than K_p , the reaction will proceed to the left. Products will be converted back into reactants.

(b) Given the reaction stoichiometry and initial conditions, we have sufficient information to set up the equilibrium expression:



	INITIAL		CHANGE		EQUILIBRIUM
P_{CO_2}	= 1.00	+	x	=	$1.00 + x$
P_{H_2}	= 1.00	+	x	=	$1.00 + x$
P_{CO}	= 1.00	-	x	=	$1.00 - x$

The partial pressures of CO_2 and H_2 (the reactants) *increase* as the system moves left toward equilibrium, whereas the partial pressure of CO (the product) decreases:

$$\frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} = K_p$$

$$\frac{1.00 - x}{(1.00 + x)(1.00 + x)} = 3.2 \times 10^{-4}$$

(c) Simplify the equation and solve:

$$\frac{1 - x}{(1 + x)^2} = K_p$$

$$1 - x = K_p (1 + x)^2 = K_p (x^2 + 2x + 1)$$

$$0 = K_p x^2 + (2K_p + 1)x + (K_p - 1)$$

The latter expression is a quadratic equation of the form

$$ax^2 + bx + c = 0$$

where

$$a = K_p = 0.00032 \quad b = 2K_p + 1 = 1.00064 \quad c = K_p - 1 = -0.99968$$

Its solution is given by the quadratic formula (see Section B-3 of *PoC*):

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 0.99872164, -3127.9987$$

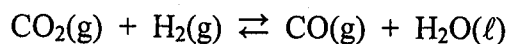
Rejecting the second root as unphysical and retaining $x = 0.9987$, we now have the final partial pressures of all species at equilibrium:

$$P_{\text{CO}_2} = P_{\text{H}_2} = 1.00 + x = 1.00 + 0.9987 = 1.9987 \text{ atm} \approx 2.00 \text{ atm}$$

$$P_{\text{CO}} = 1.00 - x = 1.00 - 0.9987 = 1.3 \times 10^{-3} \text{ atm}$$

Nearly all the CO is converted into CO_2 and H_2 .

39. Halving the volume doubles each partial pressure in the reaction under consideration:



The nonequilibrium pressures are therefore twice their former equilibrium values:

$$P_{\text{CO}_2} = 2(1.0 \text{ atm}) = 2.0 \text{ atm}$$

$$P_{\text{H}_2} = 2(1.0 \text{ atm}) = 2.0 \text{ atm}$$

$$P_{\text{CO}} = 2(3.2 \times 10^{-4} \text{ atm}) = 6.4 \times 10^{-4} \text{ atm}$$

(a) Compare the equilibrium constant

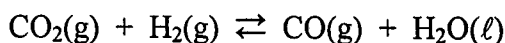
$$K_p = \frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} = 3.2 \times 10^{-4}$$

with the reaction quotient computed immediately after the volume is halved:

$$Q = \frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} = \frac{6.4 \times 10^{-4}}{(2.0)(2.0)} = 1.6 \times 10^{-4} = \frac{K_p}{2}$$

The quotient is less than K_p . To restore equilibrium, the system must move to the right.

(b) Let x denote the change in partial pressure as reactants (CO_2 and H_2) are transformed into products:



	INITIAL	CHANGE	EQUILIBRIUM
P_{CO_2}	= 2.0	- x	= 2.0 - x
P_{H_2}	= 2.0	- x	= 2.0 - x
P_{CO}	= 6.4×10^{-4}	+ x	= $6.4 \times 10^{-4} + x$

Inserting the equilibrium partial pressures into the mass-action expression, we then have the following equation to solve:

$$K_p = \frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} = \frac{6.4 \times 10^{-4} + x}{(2.0 - x)(2.0 - x)} = 3.2 \times 10^{-4}$$

To simplify appearances, we note that the number 6.4×10^{-4} happens to have the value $2K_p$:

$$\frac{2K_p + x}{(2-x)^2} = K_p$$

$$2K_p + x = K_p(2-x)^2 = K_p(4 - 4x + x^2)$$

$$2K_p + x = 4K_p - 4K_px + K_px^2$$

$$0 = K_px^2 - (4K_p + 1)x + 2K_p$$

The resulting form corresponds to a quadratic equation

$$ax^2 + bx + c = 0$$

with

$$a = K_p = 0.00032 \quad b = -(4K_p + 1) = -1.00128 \quad c = 2K_p = 0.00064$$

and solution

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 6.39181978 \times 10^{-4}, 3128.99936$$

See Section B-3 of *PoC* (Appendix B) for details on the quadratic formula.

After rejecting as unphysical the large second root (3.1×10^3) and retaining $x = 6.4 \times 10^{-4}$, we have the final partial pressures at equilibrium:

$$P_{\text{CO}_2} = 2.0 - x = 2.0 - 6.4 \times 10^{-4} = 1.9994 \text{ atm} \approx 2.0 \text{ atm}$$

$$P_{\text{H}_2} = 2.0 - x = 2.0 - 6.4 \times 10^{-4} = 1.9994 \text{ atm} \approx 2.0 \text{ atm}$$

$$P_{\text{CO}} = 6.4 \times 10^{-4} + x = 6.4 \times 10^{-4} + 6.4 \times 10^{-4} = 1.3 \times 10^{-3} \text{ atm}$$

There is a very slight readjustment of the pressures to restore equilibrium, undetectable within our range of two significant figures.

QUESTION: Since x proves to be so small, is it necessary to solve the full quadratic equation?

ANSWER: No. We obtain effectively the same result by assuming that $x \ll 2.0$ and solving a simplified linear equation:

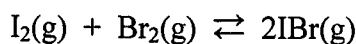
$$\frac{2K_p + x}{(2-x)^2} = K_p$$

$$\frac{2K_p + x}{2^2} \approx K_p$$

$$2K_p + x \approx 4K_p$$

$$x \approx 2K_p = 6.4 \times 10^{-4}$$

40. Here, and in Exercises 41 through 44, we consider the following reaction between iodine and bromine:



(a) Given the volume of the system and the molar amount of each component at equilibrium, we have sufficient information to calculate the final concentrations:

$$[\text{I}_2] = \frac{1.000 \text{ mol}}{100.0 \text{ L}} \quad [\text{Br}_2] = \frac{0.250 \text{ mol}}{100.0 \text{ L}} \quad [\text{IBr}] = \frac{8.972 \text{ mol}}{100.0 \text{ L}}$$

The equilibrium constant K_c follows directly:

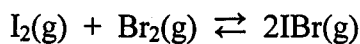
$$K_c = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = \frac{\left(\frac{8.972}{100.0}\right)^2}{\left(\frac{1.000}{100.0}\right)\left(\frac{0.250}{100.0}\right)} = 322 \quad (T = 350 \text{ K})$$

Since there are two moles of gaseous reactants and two moles of gaseous products ($\Delta n = 0$), the value of K_c is independent of volume and equal to K_p :

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} = K_c \left(\frac{c^\circ RT}{P^\circ}\right)^0 = K_c = 322$$

(b) K_c and K_p are the same because there are equal numbers of gas particles on either side of the balanced chemical equation. The mass-action ratios do not vary with volume.

41. We continue with the I_2 - Br_2 - IBr system introduced in Exercise 40,



this time with a new set of final concentrations.

(a) Use the same method as before to calculate K_c (which is equal to K_p , since $\Delta n = 0$):

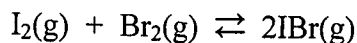
$$[\text{I}_2] = \frac{6.76 \text{ mol}}{100.0 \text{ L}} \quad [\text{Br}_2] = \frac{1.85 \text{ mol}}{100.0 \text{ L}} \quad [\text{IBr}] = \frac{63.44 \text{ mol}}{100.0 \text{ L}}$$

$$K_c = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = \frac{\left(\frac{63.44}{100.0}\right)^2}{\left(\frac{6.76}{100.0}\right)\left(\frac{1.85}{100.0}\right)} = 322 \quad (T = 350 \text{ K})$$

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ}\right)^0 = K_c = 322$$

(b) The equilibrium constant, dependent only on the temperature, has the same numerical value even though the composition of the final mixture is different.

42. The reaction is the same,



but the initial concentrations are different:

$$[\text{I}_2]_0 = [\text{Br}_2]_0 = [\text{IBr}]_0 = \frac{20.00 \text{ mol}}{100.0 \text{ L}} = 0.2000 \text{ M}$$

(a) Compute the reaction quotient and compare its value with $K = 322$, previously determined for $T = 350 \text{ K}$:

$$Q = \frac{[\text{IBr}]_0^2}{[\text{I}_2]_0[\text{Br}_2]_0} = \frac{(0.2000)^2}{(0.2000)(0.2000)} = 1.000 < K$$

The mixture is not in equilibrium at the specified temperature, since Q is unequal to K .

(b) The reaction quotient is numerically less than the equilibrium constant:

$$Q = 1.000 \quad K = 322$$

Hence the process goes to the right—to form more product (IBr) and to consume more reactants (I_2 and Br_2) until the mass-action ratio increases to 322.

43. In each of the three mixtures, the initial reaction quotient

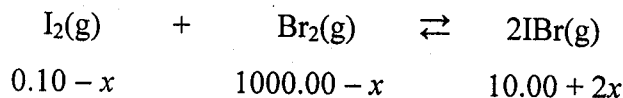
$$Q = \frac{[\text{IBr}]_0^2}{[\text{I}_2]_0[\text{Br}_2]_0}$$

is equal to 1, substantially less than the equilibrium value of 322 at $T = 350 \text{ K}$:

$$\begin{array}{ccc}
 Q_1 & Q_2 & Q_3 \\
 \frac{\left(\frac{10.00}{100.0}\right)^2}{\left(\frac{10.00}{100.0}\right)\left(\frac{10.00}{100.0}\right)} = 1.000 & \frac{\left(\frac{10.00}{100.0}\right)^2}{\left(\frac{100.00}{100.0}\right)\left(\frac{1.00}{100.0}\right)} = 1.00 & \frac{\left(\frac{10.00}{100.0}\right)^2}{\left(\frac{0.10}{100.0}\right)\left(\frac{1000.00}{100.0}\right)} = 1.0
 \end{array}$$

All of the systems must make more IBr in order to reach equilibrium, but the amounts needed will depend on the existing balance of Br_2 and I_2 .

For example, in mixture (3) there is only 0.10 mol I_2 available for reaction:



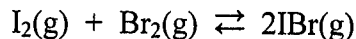
Even if nearly this entire quantity were to react, the maximum amount of IBr would be only 10.20 mol ($10.00 + 2 \times 0.10$). Thus at equilibrium we expect mixture (3) to have the following approximate composition:

slightly more than 10.00 mol IBr
slightly less than 1000.00 mol Br_2
nearly 0 mol I_2

A reaction quotient equal to 322 (the equilibrium constant, K) can be realized with amounts in these general proportions.

In mixture (1), by contrast, fully 10 moles of both Br_2 and I_2 are present at the start, and the maximum amount of IBr attainable is much greater as a result.

44. Here we consider how the equilibrium



responds to external stresses. See Section 12-6 and Examples 12-11 through 12-15.

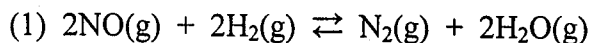
(a) *Decrease the volume of the container.* Changes in volume have no effect on the composition at equilibrium, because products and reactants are both composed of the same number of gas particles. The form and value of K remain unaltered.

- (b) *Increase the volume of the container.* Again, no effect on the equilibrium.
- (c) *Decrease the temperature.* Heat plays the role of a reactant in an endothermic process. Thus any reduction in temperature, equivalent to the removal of a reactant, will drive the reaction to the left—to consume products and regenerate reactants. Dependent on temperature, the equilibrium constant decreases as well.
- (d) *Increase the temperature.* The opposite effect: A rise in temperature, equivalent to the addition of a reactant, will drive an endothermic process to the right—to consume reactants and generate products. The equilibrium constant goes up.
- (e) *Remove IBr.* Removal of product does not change the numerical value of K , but it does pull the reaction further to the right. More products will be formed; more reactants will be consumed.
- (f) *Add IBr.* The opposite effect: Addition of product will drive the reaction to the left—in the direction that consumes IBr. The equilibrium constant remains unchanged.
- (g) *Remove Br₂.* Removal of a reactant forces the process to the left, while preserving the numerical value of K . When equilibrium is established, the mixture will contain more reactants (I₂ and Br₂) and less product (IBr) than before.
- (h) *Add Br₂.* The opposite effect: a shift to the right. Again, the numerical value of K stays the same.
- (i) *Remove I₂.* Similar to removal of Br₂, as described for (g) above.
- (j) *Add I₂.* Similar to addition of I₂, as described for (h) above.

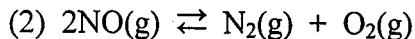
45. To begin, we determine

$$\Delta n = \text{no. moles gaseous products} - \text{no. moles gaseous reactants}$$

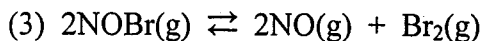
for the three reactions:



$$\Delta n = (1 + 2) - (2 + 2) = -1$$



$$\Delta n = (1 + 1) - 2 = 0$$



$$\Delta n = (2 + 1) - 2 = 1$$

(a) Changes in volume will affect only those systems for which $\Delta n \neq 0$: Processes (1) and (3) will be driven out of equilibrium. Process (2) will be unperturbed.

(b) Reduction of the volume causes the pressure to increase. The system then moves in the direction that reduces the total number of gas particles: Process (1) moves to the right, toward more products and less reactants. Process (3) moves to the left, toward more reactant and less products.

See Section 12-6 and also Examples 12-13 and 12-14 in *PoC*.

46. Equilibrium versus steady state.

(a) *Steady state*. Two arms wrestling on a tabletop, neither able to budge the other, have reached a steady state—not a true, self-sustaining equilibrium. The wrestlers maintain their stalemate by expending energy derived from external sources (food, namely). Eventually they will tire, and the balance of forces will be destroyed.

(b) *Equilibrium*. A chemical reaction in a closed vessel, with all concentrations conforming to their mass-action ratios, does persist in a true equilibrium. No material goes in, and no material goes out. The dynamic opposition of forces can be maintained indefinitely provided that external conditions (pressure, temperature, and so forth) do not change.

(c) *Steady state*. According to the description, products are removed and fresh reactants are added to maintain the fixed concentrations. The reaction must be tended.

(d) *Steady state*. Energy and matter flow into and out of the cell. Life is a nonequilibrium phenomenon.