Chapter 14: Chemical Equilibrium

In this chapter we will discuss

- What is the state of dynamic equilibrium? What are the characteristics of a system at equilibrium?
- What is the equilibrium constant, \( K \)? What does it represent?
- How do you quantify the composition of a system at equilibrium? i.e. “equilibrium composition” of a system defines the concentrations or pressures of all species present
- What system changes can cause the equilibrium position to change? i.e. predict the “shift” in equilibrium in response to changes in conditions

Until now we have considered that reactions go to completion

- identify limiting reactant (LR); assume that one reactant is completely consumed causing the reaction to stop
- calculate theoretical yield of product based on LR

But now consider: \( \text{NO}_2(g) + \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g) \)

- \( \text{NO}_2(g) \) is a reddish-brown gas; \( \text{N}_2\text{O}_4 \) is a colorless gas
- sample of \( \text{NO}_2 \) (g) sealed in a container
- initially the contents of the flask are reddish-brown; over time the intensity of the reddish-brown color decreases suggesting that \( \text{NO}_2 \) is consumed and \( \text{N}_2\text{O}_4 \) is formed; i.e. that the reaction is occurring as written
- after some time the intensity of the reddish-brown color stops changing; the contents of the flask never go to completely colorless
- conclusions: 1. reaction does not go to completion b/c \( \text{NO}_2 \) is not completely consumed (reddish-brown color still visible); 2. at some point the relative amounts of \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \), concentrations, stop changing (b/c reddish-brown color remains constant)

- \( \text{This system reaches a state of dynamic chemical equilibrium.} \)

For a system at equilibrium:

1. concentrations of reactants and products remain constant with time
2. rate of forward reaction = rate of reverse reaction
3. we refer to the “equilibrium position” of the system; i.e. whether reactants or products favored (present in larger quantity) at equilibrium

- as a system approaches equilibrium there is a lot of back and forth adjusting of concentrations and rates until conditions required by equilibrium are established
- at equilibrium reaction is still occurring; it is a \textbf{dynamic} situation
- a couple of examples:
  - car population in 2 cities connected by a bridge

The Haber Process (ammonia synthesis): \( 3 \text{H}_2(g) + \text{N}_2(g) \leftrightarrow 2 \text{NH}_3(g) \)
The equilibrium constant, \( K \)

- there is a specific mathematic relationship that exists between [products] and [reactants] at equilibrium

- Law of Mass Action, 1864, Guidberg & Waage

- consider: \( 2 \text{SO}_2 (g) + \text{O}_2 (g) \leftrightarrow 2 \text{SO}_3 (g) \) run at same temperature, but different initial reactant concentrations

<table>
<thead>
<tr>
<th>exp’t</th>
<th>([\text{O}<em>2]</em>{eq}, \text{M})</th>
<th>([\text{SO}<em>2]</em>{eq}, \text{M})</th>
<th>([\text{SO}<em>3]</em>{eq}, \text{M})</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.390</td>
<td>0.660</td>
<td>0.0840</td>
<td>0.0415</td>
</tr>
<tr>
<td>2</td>
<td>0.220</td>
<td>0.0380</td>
<td>0.00360</td>
<td>0.0409</td>
</tr>
<tr>
<td>3</td>
<td>0.110</td>
<td>0.110</td>
<td>0.00750</td>
<td>0.0423</td>
</tr>
<tr>
<td>4</td>
<td>0.880</td>
<td>0.950</td>
<td>0.180</td>
<td>0.0408</td>
</tr>
<tr>
<td>5</td>
<td>1.98</td>
<td>1.44</td>
<td>0.410</td>
<td>0.0409</td>
</tr>
</tbody>
</table>

\( K_{ave} 0.0413 \)

- \( K \) is: the equilibrium constant
  - unitless
  - dependent on specific reaction and temperature
  - independent of initial concentrations

- for this reaction:
  \[
  K_C = \frac{[\text{SO}_3]^2}{[\text{O}_2][\text{SO}_2]^2}
  \]

  for a general reaction of the form: \( a \text{A} + b \text{B} \leftrightarrow e \text{E} + g \text{G} \):
  \[
  K_C = \frac{[\text{E}]^e[\text{G}]^g}{[\text{A}]^a[\text{B}]^b}
  \]

- 2 examples:
  ex. Calculate \( K_C \) for the following reaction: \( 2 \text{CO} (g) + 2 \text{H}_2 (g) \leftrightarrow \text{CH}_4 (g) + \text{CO}_2 (g) \) if, at equilibrium, 
  \[
  [\text{CO}] = 4.30 \times 10^{-6} \text{ M}, [\text{H}_2] = 1.15 \times 10^{-3} \text{ M}, [\text{CH}_4] = 5.14 \times 10^4 \text{ M}, \text{ and } [\text{CO}_2] = 4.12 \times 10^4 \text{ M}.
  \]

  \( answer: K_C = 8.66 \times 10^{29} \)

  ex. Consider: \( 2 \text{NO} (g) + \text{O}_2 (g) \leftrightarrow 2 \text{NO}_2 (g); \ K_C = 6.9 \times 10^8 \) at 500 K. Calculate the equilibrium concentration of NO if \( [\text{NO}_2]_{eq} = 0.050 \text{ M} \) and \( [\text{O}_2]_{eq} = 1.0 \times 10^{-3} \text{ M} \)

  \( answer: [\text{NO}]_{eq} = 0.0019 \text{ M} \)

- What can you tell about a reaction from its equilibrium constant?
  - if \( K_C \) is large, [products] >> [reactants]; the reaction is said to favor the products
  - if \( K_C \) is small, [products] << [reactants]; the reaction is said to favor the reactants

Relationship between \( K \) and \( k \); equilibrium and rates of reaction

- at equilibrium \( \text{rate}_{\text{fwh}} = \text{rate}_{\text{rev}} \)

- rate is dependent on concentration; given by the rate law

- at equilibrium [reactants] and [products] must satisfy Law of Mass Action and equal \( K_C \)
Relationship between $K$'s of related reactions

- How does $K$ change if you . . .
  1. reverse the reaction?
  2. change all stoichiometric coefficients by some common factor, $n$?
  3. add 2 equations together to get a new, 3rd, net chemical equation?

Consider the following related equations:

- eqn 1: $H_2 (g) + I_2 (g) \leftrightarrow 2 HI (g)$; $K_C^1 = 54 \text{ at } 700 \text{ K}$
- eqn 2: $2 HI (g) \leftrightarrow H_2 (g) + I_2 (g)$; $K_C^2 = ??$
- eqn 3: $2 H_2 (g) + 2 I_2 (g) \leftrightarrow 4 HI (g)$; $K_C^3 = ??$

To see how $K_C^1, K_C^2$, and $K_C^3$ are related, look at the equilibrium expressions:

- $K_C^1 = \frac{[HI]^2}{[H_2][I_2]}$
- $K_C^2 = \frac{[H_2][I_2]}{[HI]^2}$
- $K_C^3 = \frac{[HI]^4}{[H_2]^2[I_2]^2}$

so, $K_C^2 = (K_C^1)^{-1} = 0.018$ and, $K_C^3 = (K_C^1)^2 = 2900$

To answer #1 above: If you reverse an equation, the equilibrium constant for the new equation is equal to the reciprocal of the 1st equilibrium constant; $K_C = 1/K_C^{\text{orig}}$.

To answer #2 above: If you multiply an equation by some factor $n$ (i.e. multiply all stoichiometric coefficients by $n$), the equilibrium constant for the new equation is equal to the 1st equilibrium constant raised to the $n$th power; $K_C = (K_C^{\text{orig}})^n$.

Consider the following related equations:

- eqn 1: $2 P (g) + 3 Cl_2 (g) \leftrightarrow 2 PCl_3 (g)$; $K_C^1$
- eqn 2: $2 PCl_3 (g) + 2 Cl_2 (g) \leftrightarrow 2 PCl_5 (g)$; $K_C^2$
- eqn 3: $2 P (g) + 5 Cl_2 (g) \leftrightarrow 2 PCl_5 (g)$; $K_C^3$

Again, to see how $K_C^1, K_C^2$, and $K_C^3$ are related, look at the equilibrium expressions:

- $K_C^1 = \frac{[PCl_3]^2}{[P]^2[Cl_2]^3}$
- $K_C^2 = \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2}$
- $K_C^3 = \frac{[PCl_5]^2}{[P]^2[Cl_2]^3}$

SO: $K_C^3 = (K_C^1)(K_C^2)$

To answer #3 above: If you add 2 (or more) equations together to get a new net chemical equation, the equilibrium constant for the new equation is equal to the product of the $K$'s of the added equations; $K_C^3 = K_C^1 x K_C^2$. 
Equilibrium constants in terms of pressures, $K_p$

- For gases, pressure and concentration are related:
  \[ PV = nRT \]
  \[ P = \frac{n}{V}RT \quad OR \quad P = M \text{(constant)} \]

- The composition of a system at equilibrium can be defined in terms of the concentration or partial pressures* of all species present

  \[ K_P = \frac{K_C(RT)^{\Delta n}}{P_{CH_4}^{a}P_{H_2S}^{b}} = 0.0042 \]

  Now, calculate $K_C$ for this reaction if the temperature above is 1000 K.
  $\Delta n = (4+1 \text{ mol product in gas phase}) - (2+1 \text{ mol reactant in gas phase}) = 2$

  \[ \text{answer: } 6.2 \times 10^{-7} \]

Heterogeneous Equilibria

- Reactants and products are not all in the same phase

  Very common examples:
  - Phase change equilibria: $H_2O (l) \leftrightarrow H_2O (g)$
  - Solubility equilibria: $AgCl (s) \leftrightarrow Ag^+ (aq) + Cl^- (aq)$

  Weak acid equilibria: $HF (aq) + H_2O (l) \leftrightarrow F^- (aq) + H_3O^+ (aq)$

  \[ \text{note: Get used to seeing these!!} \]

- The bottom line: Pure solids, indicated by (s), and pure liquids, indicated by (l), are not included in the equilibrium expression.

- You only include in the equilibrium expression species whose concentration can change.

- Equilibrium expressions for the reactions above are:

  \[ K_P = \frac{P_{H_2O}}{P_{CH_4}P_{H_2S}^{4}} \]

  \[ K_C = [Ag^+][Cl^-] \]

  \[ K_C = \frac{[F^-][H_3O^+]}{[HF]} \]

Determining the direction of reaction; $Q$ vs $K$

- At some point after a reaction has started, how do you know if the amounts of substances present represent an equilibrium mixture? Or does further forward reaction have to occur to reach equilibrium? Or, has the reaction gone farther forward than the equilibrium position and need to proceed in the reverse direction to reach equilibrium?

- The answer to all of these questions involves predicting the direction of reaction.

- To predict the direction of reaction, calculate $Q$ (the reaction quotient) and compare $Q$ to $K$.

  - If $Q = K$, the system is at equilibrium
  - If $Q < K$, the system is not at equilibrium and reaction will proceed forward toward equilibrium
  - If $Q > K$, the system is not at equilibrium and reaction will proceed in reverse toward equilibrium

- For a reaction $aA + bB \leftrightarrow eE + gG$,
  \[ Q_C = \frac{[E]^e[G]^g}{[A]^a[B]^b} \]

  OR

  \[ Q_P = \frac{P_{E}^{e}P_{G}^{g}}{P_{A}^{a}P_{B}^{b}} \]
So what is the difference between Q and K if they are calculated the same way?

K is defined by equilibrium concentrations or pressures; the concentrations or pressures used to calculate Q are arbitrary - they do not necessarily represent an equilibrium mixture.

Equilibrium Calculations; using an equilibrium (ICE) table

mainly 2 types of problems:
1. determination of the equilibrium composition (in [ ] or P) of the system
2. determination of K_c (or K_p)

ex. for the reaction: 2A + B ⇌ 3C

<table>
<thead>
<tr>
<th></th>
<th>2 A</th>
<th>+</th>
<th>B</th>
<th>⇌</th>
<th>3 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial [ ] or P</td>
<td>1.00 M</td>
<td>2.00 M</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ</td>
<td>- 2x</td>
<td>- x</td>
<td>+ 3x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>equil [ ] or P</td>
<td>(1.00 - 2x) M</td>
<td>(2.00 - x) M</td>
<td>3x M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Consider the same reaction from 2 different perspectives: SO_2 (g) + NO_2 (g) ⇌ SO_3 (g) + NO (g)
1.24 mol SO_2 and 0.750 mol NO_2 combined in a 2.50 L flask

Perspective 1: the old way – assuming the reaction goes to completion
identify the limiting and excess reactants; calculate theoretical yield
using a reaction table:

<table>
<thead>
<tr>
<th></th>
<th>SO_2 (g)</th>
<th>+</th>
<th>NO_2 (g)</th>
<th>⇌</th>
<th>SO_3 (g)</th>
<th>+</th>
<th>NO (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol before rxn</td>
<td>1.24 mol</td>
<td>0.750 mol</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ mol</td>
<td>- 0.750 mol</td>
<td>- 0.750 mol</td>
<td>+ 0.750 mol</td>
<td>+ 0.750 mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mol after rxn</td>
<td>0.49 mol</td>
<td>0</td>
<td>0.750 mol</td>
<td>0.750 mol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NO_2 is the limiting reactant; SO_2 is the excess reactant; theoretical yield of SO_3 and NO = .750 mol each

Perspective 2: the new way – understanding that the system reaches equilibrium
for this reaction, K_c = 3.75
[SO_2]_0 = 1.24 mol/2.50 L = 0.496 M  [NO_2]_0 = 0.0750 mol/2.50 L = 0.300 M

using an equilibrium table:

<table>
<thead>
<tr>
<th></th>
<th>SO_2 (g)</th>
<th>+</th>
<th>NO_2 (g)</th>
<th>⇌</th>
<th>SO_3 (g)</th>
<th>+</th>
<th>NO (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial [ ]</td>
<td>0.496 M</td>
<td>0.300 M</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ [ ]</td>
<td>- x</td>
<td>- s</td>
<td>+ x</td>
<td>+ x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equil [ ]</td>
<td>(0.496 - x) M</td>
<td>(0.300 - x) M</td>
<td>x M</td>
<td>x M</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

now, solve for x; once you know x you can calculate the equilibrium [ ] of each species

K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} \quad 3.75 = \frac{(x)(x)}{(0.496 - x)(0.300 - x)} = \frac{x^2}{0.149 - 0.796x + x^2}

get this into the form of ax^2 + bx + c and solve for x using the quadratic formula
in this example: 2.75x^2 - 2.99x + 0.559 = 0; a = 2.75, b = -2.99, c = 0.559
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}; \text{ here } x = 0.847 \text{ OR } 0.240$$

**note:** both of these solutions are valid mathematically, but only one is valid in this problem; the other is called the extraneous root

**and:** in this problem 0.847 is the extraneous root because when plugged into either .496 — x or .300 — x the answer is negative; it is not possible to have a negative concentration or pressure (i.e. negative matter)

$$x = 0.240 \therefore \text{ at equilibrium: } [\text{SO}_2] = .496 - x = 0.256 \text{ M}$$
$$[\text{NO}_2] = .300 - x = 0.060 \text{ M}$$
$$[\text{SO}_3] = [\text{NO}] = x = 0.240 \text{ M}$$

Comparing the two perspectives:
if you compare, for example, the results for mol of SO$_3$ present after reaction, perspective 1 predicts 0.750 mol and perspective 2 predicts (more accurately) 0.60 mol (0.240 mol/L but in a 2.50 L flask)

this is $\approx 23\%$ error if you treat the reaction as if it goes to completion instead of applying the concept of dynamic chemical equilibrium

**example 2:** determination of equilibrium composition (using $K_p$ and $P$’s)
Consider the water-gas shift reaction: CO (g) + H$_2$O (g) $\leftrightarrow$ CO$_2$ (g) + H$_2$ (g); $K_p = K_C = 4.24$ at 800 K.

Determine the equilibrium composition of this system if the initial pressures of CO and H$_2$O are 12.0 atm each.

set up the equilibrium table:

<table>
<thead>
<tr>
<th></th>
<th>CO (g)</th>
<th>H$_2$O (g)</th>
<th>$\leftrightarrow$</th>
<th>CO$_2$ (g)</th>
<th>H$_2$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>initial P</strong></td>
<td>12.0 atm</td>
<td>12.0 atm</td>
<td>0 atm</td>
<td>0 atm</td>
<td></td>
</tr>
<tr>
<td><strong>$\Delta P$</strong></td>
<td>$-x$</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td><strong>equil P</strong></td>
<td>$(12.0-x)$ atm</td>
<td>$(12.0-x)$ atm</td>
<td>$x$ atm</td>
<td>$x$ atm</td>
<td></td>
</tr>
</tbody>
</table>

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = 4.24 = \frac{x^2}{(12.0 - x)^2}$$

this is a perfect square; to solve for $x$, take $\sqrt{\text{of both sides}}$

$$x = 8.07; \text{ at equilibrium: } P_{CO_2} = P_{H_2} = x \text{ atm} = 8.07 \text{ atm}$$
$$P_{CO} = P_{H_2O} = 12.0 - x \text{ atm} = 3.93 \text{ atm}$$

**example 3:** determination of equilibrium composition using arbitrary initial data

Determine the equilibrium composition for the following reaction: N$_2$O$_4$ (g) $\leftrightarrow$ 2 NO$_2$ (g); $K_C = 4.64 \times 10^{-3}$

if $[\text{N}_2\text{O}_4] = 0.0200 \text{ M}$ and $[\text{NO}_2] = 0.0300 \text{ M}.$

The concentration data in this problem is called “arbitrary initial data” because it is the first thing you know about the system (i.e. initial), but not true initial data (i.e. arbitrary).

1st determine if this system is at equilibrium. Calculate $Q_C$, compare to $K_C$.

$$Q_C = 0.045; Q_C > K_C \therefore \text{ the system is not at equilibrium, and the reaction will proceed in reverse to reach equilibrium}$$

set up the equilibrium table; note the difference in the $\Delta [\ ]$ row here as the reaction proceeds in reverse
equilibrium calculation, example 4: determination of K from experimental data

Consider the reaction: \( \text{H}_2 (g) + \text{I}_2 (g) \leftrightarrow 2 \text{HI} (g) \). 0.750 M \( \text{H}_2 \) and 0.990 M \( \text{I}_2 \) were combined in a flask and the system was allowed to reach equilibrium. At equilibrium, \([\text{I}_2] = 0.330 \text{ M}\). Determine the value of \( K_C \).

set up the table . . .

| \( \text{H}_2 \) (g) | + | \( \text{I}_2 \) (g) | \( \leftrightarrow \) | 2 \( \text{HI} \) (g) |
|---------------------|---|---------------------|------------------|
| initial [ ]         | .750 M | .990 M | 0 M |
| \( \Delta \) [ ]    | \( -x \) | \( +2x \) |
| equil [ ]           | \( (.750-x) \text{ M} \) | \( (.990-x) \text{ M} \) | \( 2x \text{ M} \) |

What do we know?  
- at equil \([\text{I}_2] = 0.990 - x \text{ M}\) (from table) AND at equil \([\text{I}_2] = 0.330 \text{ M}\) (given data)
- solve for \( x \) . . .  
  \[ 0.990 - x = 0.330 \]  
  \[ ∴ x = 0.660 \]
- use \( x \) to determine \([\text{H}_2]\) and \([\text{HI}]\) at equilibrium  
  \[ \text{answer: } [\text{H}_2] = 0.090 \text{ M}, [\text{HI}] = 1.32 \text{ M} \]
- use equilibrium concentrations to solve for \( K_C \)  
  \[ \text{answer: } K_C = 58.7 \]

Le Chatelier’s Principle

- If a stress is applied to a system at equilibrium, the equilibrium position will shift in the direction that relieves that stress.

- **Goal:** to understand how experimental changes affect changes in the equilibrium position
  - predict the effect of:
    - changing reactant or product concentration
    - changing system pressure (as a result of changing system volume)
    - changing temperature
    - addition of catalyst

- **Concentration**
  - If the equilibrium is disturbed by the addition or removal of reactant or product, Le Chatelier’s Principle predicts:
    1. If the concentration of reactant or product is increased (i.e. by addition) the equilibrium position will shift in the direction that consumes the added substance (i.e. away from the increased concentration).
    2. If the concentration of reactant or product is decreased (i.e. by removal) the equilibrium position will shift in the direction that replenishes the removed substance (i.e. toward the decreased concentration).

- **Pressure or Volume**
  - There are essentially 3 ways to change the pressure of a chemical reaction system:
    1. add or remove a gas phase reactant or product
      - recall that \( P_{\text{reactant}} \) or \( P_{\text{product}} \) are related (through \( PV=nRT \)) to molar concentration
      - the result of adding or removing gas phase reactant or product can be predicted according to the guidelines stated above for effect of changing concentration.
2. add an inert gas
   The addition of an inert gas to a system changes the total pressure of the system, but not the partial pressures (i.e. changing concentrations) of gas phase reactants or products. The result is no change in equilibrium position.

3. change the volume of the container
   Recall that pressure and volume are inversely proportional to one another.
   If the equilibrium is disturbed by changing the volume of the container, Le Chatelier’s Principle predicts:
   I. An increase in pressure resulting from reduced container volume will bring about net reaction in the direction that decreases the number of moles of gas phase species (i.e. the volume of the chemical system will decrease).
   II. A decrease in pressure resulting from increased container volume will bring about net reaction in the direction that increases the number of moles of gas phase species (i.e. the volume of the chemical system will increase).

Temperature
   The temperature dependence of the equilibrium position and the value of the equilibrium constant is dependent on the sign of ΔH° of the reaction.
   1. The equilibrium constant for an exothermic reaction will decrease as temperature increases; equilibrium position will shift to the left as temperature increases.
   2. The equilibrium constant for an endothermic reaction will increase as temperature increases; equilibrium position will shift to the right as temperature increases.

Catalyst
   The addition of a catalyst does not effect the equilibrium position of a reaction – only the rate at which the system reaches equilibrium.

Example: Consider the equilibria presented below, and apply Le Chatelier’s principle to predict the effect of each change on the indicated quantity. Circle I, D, or N to indicate an increase, decrease, or no change in the quantity. Assume that each change is made independently to the system at equilibrium.

<table>
<thead>
<tr>
<th>reaction</th>
<th>change</th>
<th>quantity</th>
<th>prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. H₂ (g) + Cl₂ (g) ↔ 2 HCl (g)</td>
<td>add H₂</td>
<td>P_{Cl₂}</td>
<td>I D N</td>
</tr>
<tr>
<td>b. H₂ (g) + Cl₂ (g) ↔ 2 HCl (g)</td>
<td>add HCl</td>
<td>K_p</td>
<td>I D N</td>
</tr>
<tr>
<td>c. H₂ (g) + Br₂ (l) ↔ 2 HBr (g)</td>
<td>remove some H₂</td>
<td>mass of Br₂</td>
<td>I D N</td>
</tr>
<tr>
<td>d. H₂ (g) + Br₂ (l) ↔ 2 HBr (g)</td>
<td>add Br₂ (l)</td>
<td>P_{HBr}</td>
<td>I D N</td>
</tr>
<tr>
<td>e. HCOOH (aq) ↔ H⁺ (aq) + HCOO⁻ (aq)</td>
<td>reduce pH</td>
<td>[HCOO⁻]</td>
<td>I D N</td>
</tr>
<tr>
<td>f. HCOOH (aq) ↔ H⁺ (aq) + HCOO⁻ (aq)</td>
<td>add OH⁻ (aq)</td>
<td>[HCOO⁻]</td>
<td>I D N</td>
</tr>
<tr>
<td>g. HCOOH (aq) ↔ H⁺ (aq) + HCOO⁻ (aq)</td>
<td>add HCOOH</td>
<td>pK_a</td>
<td>I D N</td>
</tr>
<tr>
<td>h. PbBr₂ (s) ↔ Pb²⁺ (aq) + 2 Br⁻ (aq)</td>
<td>add PbBr₂ (s)</td>
<td>[Br⁻]</td>
<td>I D N</td>
</tr>
<tr>
<td>i. PbBr₂ (s) ↔ Pb²⁺ (aq) + 2 Br⁻ (aq)</td>
<td>add Pb(NO₃)₂ (aq)</td>
<td>[Br⁻]</td>
<td>I D N</td>
</tr>
<tr>
<td>j. PbBr₂ (s) ↔ Pb²⁺ (aq) + 2 Br⁻ (aq)</td>
<td>increase T</td>
<td>[Br⁻]</td>
<td>I D N</td>
</tr>
</tbody>
</table>

*note*reaction in h, i, and j is endothermic