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Analytical chemistry

studies and uses instruments and methods to , identify, and quantify matter. In practice, separation, identification or quantification may constitute the entire analysis or be combined with another method

1.Qualitative analysis

Qualitative analysis determines the presence or absence of a particular compound, but not the mass or concentration. By definition, qualitative analyses do not measure quantity.

2.Quantitative analysis

Quantitative analysis is the measurement of the quantities of particular chemical constituents present in a substance. Quantities can be measured by mass (gravimetric analysis) or volume (volumetric analysis).

A.Gravimetric analysis

The gravimetric analysis involves determining the amount of material present by weighing the sample before and/or after some transformation. A common example used in undergraduate education is the determination of the amount of water in a hydrate by heating the sample to remove the water such that the difference in weight is due to the loss of water.

B.Volumetric analysis

Titration involves the addition of a reactant to a solution being analyzed until some equivalence point is reached. Often the amount of material in the solution being analyzed may be determined. Most familiar to those who have taken chemistry during secondary education is the acid-base titration involving a color-changing indicator. There are many other types of titrations, for example, potentiometric titrations. These titrations may use different types of indicators to reach some equivalence point.

C.Instrumental methods

Spectroscopy measures the interaction of the molecules with Electromagnetic spectrum. Spectroscopy consists of many different applications such as Atomic absorption spectroscopy, Emission spectroscopy, Ultraviolet-visible spectroscopy X-ray spectroscopy, Fluorescence spectroscopy, Infrared spectroscopy, Nuclear magnetic resonance spectroscopy and Raman spectroscopy .

Buffer solution:-

A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base, or vice versa. Its pH changes very little when a small amount of strong acid or base is added to it.

What is a **buffer system**?

Buffers are solutions that resist a change in pH on dilution of small amounts acidic or basic substance. Buffers are extremely useful in these systems to maintain the pH at a constant value. This does not mean that the pH of buffers does not change. It only means that the change in pH is not as much as it would be with a solution that is not a buffer. What do you think will happen if the pH of our blood changes drastically from its normal pH of 7.35? Yes, the cells of our body will not function properly and our body systems will fail! Human blood contains a 'buffer' that allows it to maintain its pH at 7.35 to ensure normal functioning of . Buffer solutions are also important in chemical and biochemical processes where the control of pH is very important.

What is buffer solution example?

For **example (1)** a mixture of acetic acid and sodium acetate acts as a **buffer solution** with a pH of about 4.75. ...

For **example (2)** a mixture of ammonium chloride and ammonium hydroxide acts as a **buffer solution** with a pH of about 9.25. **Buffer solutions** help maintain the pH of many different things.

What is a buffer solution used for?

A **buffer** is a **solution** that can resist pH change upon the addition of an acidic or basic components. It is able to neutralize small amounts of added acid or base, thus maintaining the pH of the **solution** relatively stable. This is important for processes and/or reactions which require specific and stable pH ranges.

Buffer Action

So, how does a buffer work? Let's take the example of a acetic acid (CH_3COOH) and sodium acetate (CH_3COONa). Here, acetic acid is weakly ionized while sodium acetate is almost completely ionized. The equations are given as follows:

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

CH_3COONa --❼ $Na^+ + CH_3COC^-$

To this, if you add a drop of a strong acid like HCl, the H^+ ions from HCl combine with CH_3COO^- to give CH_3COOH. Thus, there is a very slight change in the pH value. Now, if you add a drop of NaOH, the OH^- ions react with the free acid to give undissociated

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

In this way, the OH^- of NaOH are removed and the pH is almost unaltered.

Classification of Buffers

There are two major classifications of buffer systems. This distinction is made on the basis of the buffer solution's pH, and the two types are:

- Acidic Buffers
- Alkaline Buffers

Buffer System Examples

As previously mentioned, a buffer is a solution of either a weak acid and its salt, or a weak base and its salt. This is why there are a wide variety of possible mixtures that can act as a buffer. Some examples of well-known buffers include:

- Acetic acid with sodium acetate
- Ammonium hydroxide with ammonium chloride
- Citric acid with sodium citrate
- Carbonic acid with bicarbonate ion

Calculating pH of Buffer

The pH of a buffer solution is calculated using the Henderson-Hasselbalch equation. The equation used differs slightly between acidic and alkaline buffers. For acidic buffers it is $pH = pKa + log10 ((A-)/(HA))$:

- pKa = Negative logarithm of the Ka (Dissociation constant for the weak acid)
- $(A-)$ = Concentration of conjugate base
- (HA) = Concentration of weak acid

for basic buffers it is $pH = pKb + log10 ((B+)/(BOH))$.

- *pKb* = Negative logarithm of the *Kb* (Dissociation constant for the weak base)
- *(B+)* = Concentration of conjugate acid
- *(BOH)* = Concentration of weak base
-

- The pH of a buffer solution can be calculated using: The K_a of the weak acid. The equilibrium concentration of the weak acid and its conjugate base (salt)
- To determine the pH, the concentration of hydrogen ions is needed which can be found using the equilibrium expression.

Is blood a buffer?

Blood. Human **blood** contains a **buffer** of carbonic acid (H_2CO_3) and bicarbonate anion (HCO_3^-) in order to maintain **blood** pH between 7.35 and 7.45, as a value higher than 7.8 or lower than 6.8 can lead to death. In this **buffer**, hydronium and bicarbonate anion are in equilibrium with carbonic acid.

What is a buffer and how does it work in the blood?

Buffers in the Human Body help maintain the bloods pH at 7.4. If blood pH falls below 6.8 or rises above 7.8, one can become sick or die.
The **bicarbonate** neutralizes excess acids in the blood while the **carbonic acid** neutralizes excess bases

What is the buffer system in blood?

Buffer Systems in the Body. ... The **buffer systems** functioning in **blood** plasma include plasma proteins, phosphate, and bicarbonate and carbonic acid **buffers**. The kidneys help control acid-base balance by excreting hydrogen ions and generating bicarbonate that helps maintain **blood** plasma pH within a normal range.

How is pH maintained in the body?

The lungs control your **body's pH** balance by releasing carbon dioxide. Carbon dioxide is a slightly acidic compound. ... Your brain constantly monitors this in order to **maintain** the proper **pH** balance in your **body**. The kidneys help the lungs **maintain** acid-base balance by excreting acids or bases into the blood.

Saturation Degree

Unsaturated Solution – less than the maximum amount of solute for a given temperature is dissolved in the solvent. – There is more available space for solute to dissolve in the solvent – No solid remains in flask. •

Saturated solution – Is one where the concentration is at a maximum - no more solute is able to dissolve (you begin to see some crystals) at that temperature. – A saturated solution represents an equilibrium. •

Supersaturated – Solvent holds more solute than is normally possible at that temperature. – You can see a big amount of solute at the bottom of the flask.

Ways of Expressing Concentration

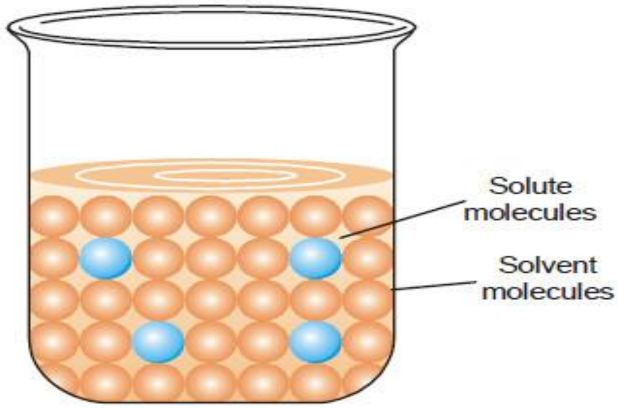
Concentration of A Solution

– The concentration of a solution is defined as : the amount of solute present in a given amount of solution.

– Concentration is generally expressed as the quantity of solute in a unit volume of solution.

A solution containing a relatively low concentration of solute is called Dilute solution.

– A solution of high concentration is called Concentrated solution.



Molecular model of a solution.

Ways of Expressing Concentration

– There are several ways of expressing concentration of a solution:

(a) Percent by weight

(b) Mole fraction

(c) Molarity

(d) Molality

(e) Normality

1) Percent by Weight

It is the **weight of the solute as a per cent of the total weight of the solution.**
That is,

$$\% \text{ by weight of solute} = \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

Solved problem on percent by Weight

What is the per cent by weight of NaCl if 1.75 g of NaCl is dissolved in 5.85 g of water?

SOLUTION

$$\begin{aligned}
\text{Wt. of solute (NaCl)} &= 1.75\text{ g} \\
\text{Wt. of solvent }(H_2O) &= 5.85\text{ g} \\
\therefore \quad \text{Wt. of solution} &= 1.75 + 5.85 = 7.60\text{ g}
\end{aligned}$$

Hence concentration of NaCl % by weight

$$= \frac{1.75}{7.60} \times 100$$
$$= \mathbf{23.0}$$

(2) Mole Fraction

– A simple solution is made of two substances : one is the solute and the other solvent.

– Mole fraction, X, of solute is defined as **the ratio of the number of moles of solute and the total number of moles of solute and solvent**.
Thus,

$$X_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

If (n) represents moles of solute and N number of moles of solvent,

$$X_{\text{solute}} = \frac{n}{n + N}$$

Notice that mole fraction of solvent would be

$$X_{\text{solvent}} = \frac{N}{n + N}$$

Mole fraction is unitless and

$$X_{solute} + X_{solvent} = 1$$

Solved problem on Mole fraction

Calculate the mole fraction of HCl in a solution of hydrochloric acid in water, containing (36)g HCl , (64)g H2O. M.Wt=(36.5 , 18)g/mol for HCl and H2O.
SOLUTION

$$\text{Number of Moles of HCl} = (36\text{ g HCl})\left(\frac{1\text{mol HCl}}{36.5\text{ g HCl}}\right) = 0.99$$

$$\text{Number of Moles of } H_2O = (64\text{ g } H_2O)\left(\frac{1\text{mol } H_2O}{18\text{ g } H_2O}\right) = 3.55$$

$$X_{HCl} = \frac{\text{moles of HCl}}{\text{moles of HCl} + \text{moles of } H_2O} = \frac{0.99}{3.55 + 0.99} = \mathbf{0.218}$$

(3) Molarity

– In current practice, concentration is most often expressed as molarity.
– Molarity (symbol M) is defined as **the number of moles of solute per litre of solution.**
– If (n) is the number of moles of solute and (V) litres the volume of solution,

M=n / V(L) =Moles/ litres

Calculation of Molarity

– Molarity of a solution can be calculated with the help of the expression (1) if moles of solute (n) and volume V (in litres) are known.

– When the amount of solute is given in grams and its molecular weight is MW, it can be converted to moles :

Substituting in expression $M = n / V$

– From the equation ($M = n / V$) can also be found the amount of solute in grams if molarity is given.

Solved problem on Molarity

Problem(1): What is the molarity of a solution prepared by dissolving 75.5 g of pure KOH in 540 ml of solution?

Problem(2): What weight of HCl is present in 155 ml of a 0.540 M solution?

(4) Molality

Molality of a solution (symbol m) is defined as **the number of moles of solute per kilogram of solvent:**

$$m = n(solute)/Kg(solvent)$$

– A solution obtained by dissolving one mole of the solute in 1000 g of solvent is called one molality or 1m solution.

– Notice the difference between molality and molarity.

– **Molality is defined in terms of mass of solvent while molarity is defined in terms of volume of solution**.

Solved problem on Molality

What is the molality of a solution prepared by dissolving 5.0 g of toluene (C_7H_8) in 225 g of benzene (C_6H_6)?
SOLUTION

(5) Normality

normality of a solution (symbol N) is defined as **number of equivalents of solute per litre of the solution.**

Solved problem on Normality

5 g of NaCl is dissolved in 1000 g of water. If the density of the resulting solution is 0.997 g per ml, calculate the molality, molarity, normality and mole fraction of the solute, assuming volume of the solution is equal to that of solvent.

Accuracy

The ability of an instrument to measure the accurate value is known as accuracy. In other words, it is the ***the closeness of the measured value to a standard or true value***. Accuracy is obtained by taking small readings. The small reading reduces the error of the calculation.

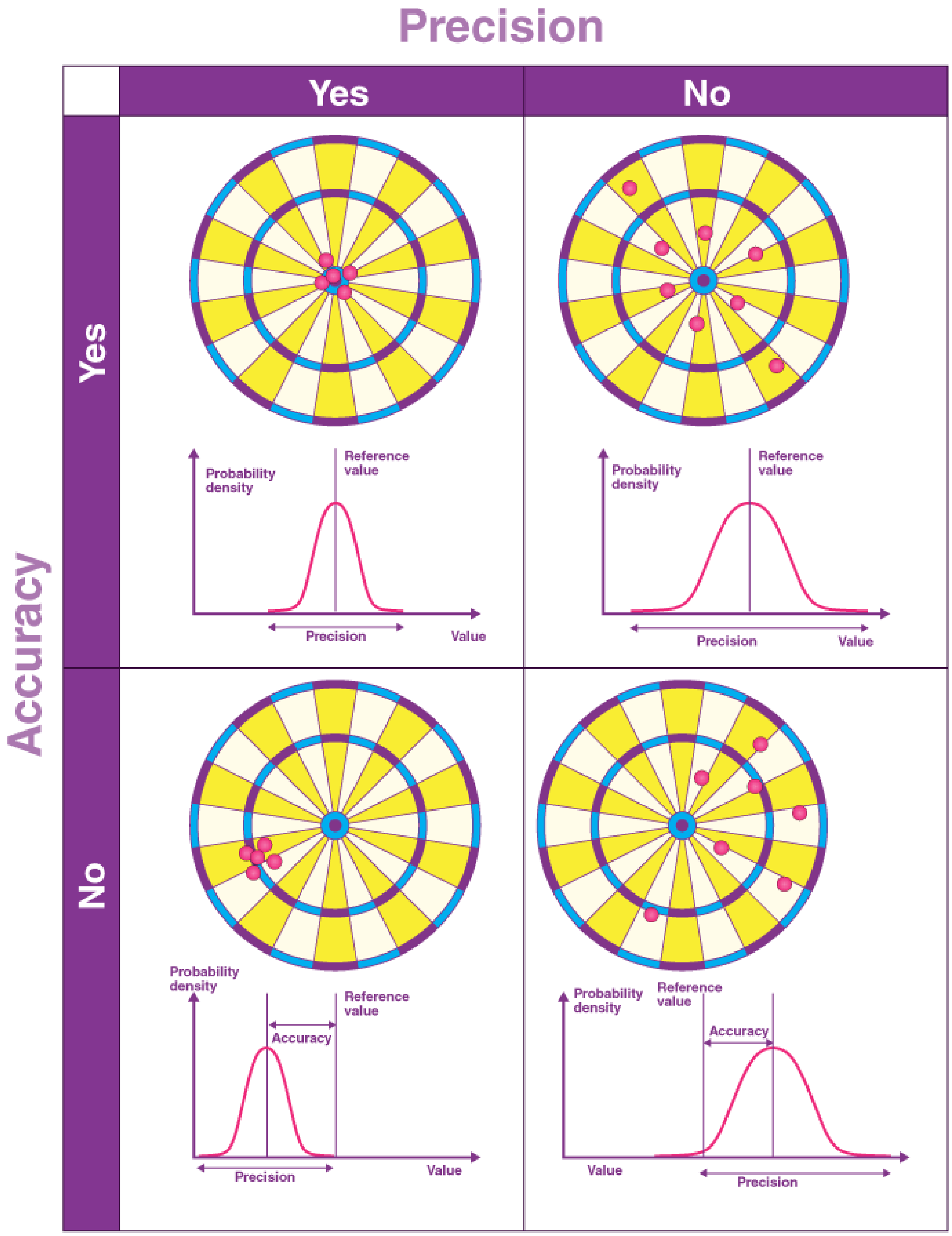
Precision

The closeness of two or more measurements to each other is known as the precision of a substance.

Accuracy and Precision Examples

A good analogy for understanding accuracy and precision is to imagine a football player shooting at the goal. If the player shoots into the goal, he is said to be accurate. A football player who keeps striking the same goalpost is precise but not accurate. Therefore, a football player can be accurate without being precise if he hits the ball all over the place but still scores. A precise player will hit the ball to the same spot repeatedly, irrespective of whether he scores or not. A precise and accurate football player will not only aim at a single spot but also score the goal.

The top left image shows the target hit at high precision and accuracy. The top right image shows the target hit at a high accuracy but low precision. The bottom left image shows the target hit at a high precision but low accuracy.



The bottom right image shows the target hit at low accuracy and low precision.

Practice Questions

Q1) The volume of a liquid is 26 mL. A student measures the volume and finds it to be 26.2 mL, 26.1 mL, 25.9 mL, and 26.3 mL in the first, second, third, and fourth trial, respectively. Which of the following statements is true for his measurements?

a. They are neither precise nor accurate.
b. They have poor accuracy.
c. They have good precision.
d. They have poor precision.

Answer: They have good precision.

Q2) The volume of a liquid is 20.5 mL. Which of the following sets of measurement represents the value with good accuracy?
18.6 mL, 17.8 mL, 19.6 mL, 17.2 mL
19.2 mL, 19.3 mL, 18.8 mL, 18.6 mL
18.9 mL, 19.0 mL, 19.2 mL, 18.8 mL
20.2 mL, 20.5 mL, 20.3 mL, 20.1 mL

Answer: The set 20.2 mL, 20.5 mL, 20.3 mL, 20.1 mL represents the value with good accuracy.

Standard deviation

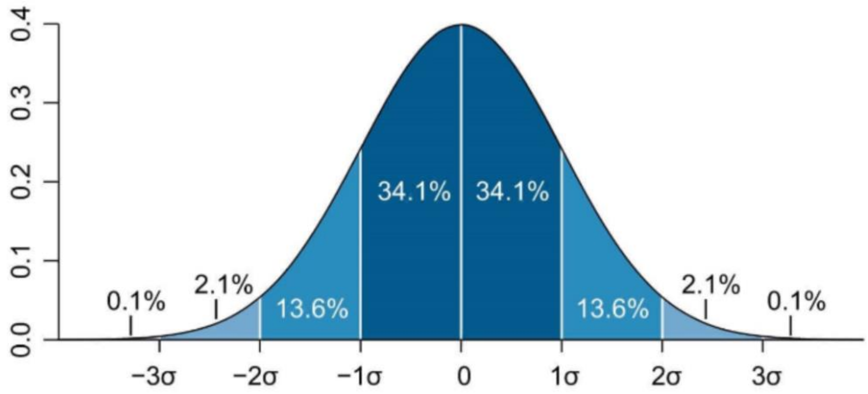
The **standard deviation** is the average amount of variability in your data set. It tells you, on average, how far each value lies from the mean.

A high standard deviation means that values are generally far from the , while a low standard deviation indicates that values are clustered close to the mean.

What is the standard deviation?

A measure of the extent to which numbers are spread out.
Standard Deviation is a statistic that measures the dispersion of a dataset

relative to its mean and is calculated as the square root of the variance. It is denoted by the Greek symbol sigma σ.
Below, you can find the plot of a normal distribution with a width of 1 band.



Equilibrium Expression

The **equilibrium expression** for a chemical reaction may be expressed in terms of the concentration of the products and reactants.

the concentrations of liquids and solids does not change. For the chemical reaction:

jA + kB → lC + mD

The equilibrium expression is

$K = ([C]^l[D]^m) / ([A]^j[B]^k)$

Factors That Affect Chemical Equilibrium

First, consider a factor that does not affect equilibrium: pure substances. If a pure liquid or solid is involved in equilibrium, it is considered to have an equilibrium constant of 1 and is excluded from the equilibrium constant. For example, except in highly concentrated solutions, pure water is considered to have an activity of 1. Another example is solid carbon, which may be form by the reaction of two carbon monoxide molecules to form carbon dioxide and carbon.

Factors that do affect equilibrium include:

- Adding reactant or product or a change in concentration affects equilibrium. Adding reactant can drive equilibrium to the right in a chemical equation, where more product forms. Adding product can drive equilibrium to the left, as more reactant forms.

- Changing the temperature alters equilibrium. Increasing temperature always shifts chemical equilibrium in the direction of the endothermic reaction. Decreasing temperature always shifts equilibrium in the direction of the exothermic reaction.
- Changing the pressure affects equilibrium. For example, decreasing the volume of a gas system increases its pressure, which increases the concentration of both reactants and products. The net reaction will see to lower the concentration of gas molecules.

Equilibrium Constant of Activities

The thermodynamically correct equilibrium constant expression relates the activities of **all** of the species present in the reaction. Although the concept of activity is too advanced for a typical General Chemistry course, it is essential that the explanation of the derivation of the equilibrium constant expression starts with activities so that no misconceptions occur. For the hypothetical reaction:

$$bB+cC \rightleftharpoons dD+eE$$

- If $K>1$ then equilibrium favors products
- If $K<1$ then equilibrium favors the reactants

Equilibrium Constant of Pressure

Gaseous reaction equilibria are often expressed in terms of partial pressures. The equilibrium constant of pressure gives the ratio of pressure of products over reactants for a reaction that is at equilibrium (again, the pressures of all species are raised to the powers of their respective coefficients). The equilibrium constant is written as Kp, as shown for the reaction:

$$aA_{(g)}+bB_{(g)} \rightleftharpoons gG_{(g)}+hH_{(g)}$$

Where p can have units of pressure (e.g., atm or bar).

Conversion of K_c to K_p

To convert K_c to K_p, the following equation is used:

$$K_p = K_c(RT)^{\Delta n_{gas}}$$

where:

- $R = 0.0820575$ L atm mol^{-1} K^{-1} or 8.31447 J mol^{-1} K^{-1}
- T= Temperature in Kelvin
- Δn_{gas}= Moles of gas (product) - Moles of Gas (Reactant)

Question 1

An equilibrium constant with a value $K > 1$ means:
a. there are more reactants than products at equilibrium
b. there are more products than reactants at equilibrium
c. there are the same amount of products and reactants at equilibrium
d. the reaction is not at equilibrium

Question 2

Equal amounts of reactants are poured into a suitable container. Given sufficient time, the reactants may be converted almost entirely to products if:
a. K is less than 1
b. K is greater than 1
c. K is equal to 1
d. K is equal to 0

Question 3

The equilibrium constant for the reaction
H_2 (g) + I_2 (g) $\leftrightarrow$ 2 HI (g)
would be:
a. $K = [HI]^2/[H_2][I_2]$
b. $K = [H_2][I_2]/[HI]^2$
c. $K = 2[HI]/[H_2][I_2]$
d. $K = [H_2][I_2]/2[HI]$

Question 4

The equilibrium constant for the reaction
2 SO_2 (g) + O_2 (g) $\leftrightarrow$ 2 SO_3 (g)
would be:
a. $K = 2[SO_3]/2[SO_2][O_2]$
b. $K = 2[SO_2][O_2]/[SO_3]$

c. $K = [SO_3]^2/[SO_2]^2[O_2]$
d. $K = [SO_2]^2[O_2]/[SO_3]^2$

Question 5

The equilibrium constant for the reaction
$Ca(HCO_3)_2$ (s) ⟷ CaO (s) + 2 CO_2 (g) + H_2O (g)
would be:
a. $K = [CaO][CO_2]^2[H_2O]/[Ca(HCO_3)_2]$
b. $K = [Ca(HCO_3)_2]/[CaO][CO_2]^2[H_2O]$
c. $K = [CO_2]^2$
d. $K = [CO_2]^2[H_2O]$

Question 6

The equilibrium constant for the reaction
SnO_2 (s) + 2 H_2 (g) ⟷ Sn (s) + 2 H_2O (g)
would be:
a. $K = [H_2O]^2/[H_2]^2$
b. $K = [Sn][H_2O]^2/[SnO][H_2]^2$
c. $K = [SnO][H_2]^2/[Sn][H_2O]^2$
d. $K = [H_2]^2/[H_2O]^2$

Question 7

For the reaction
H_2 (g) + Br_2 (g) ⟷ 2 HBr (g),
K = 4.0×10^{-2}. For the reaction
2 HBr (g) ⟷ H_2 (g) + Br_2 (g)
K =:
a. 4.0×10^{-2}
b. 5
c. 25
d. 2.0×10^{-1}

Question 8

At a certain temperature, K = 1 for the reaction
2 HCl (g) → H_2 (g) + Cl_2 (g)
At equilibrium, you can be certain that:
a. $[H_2] = [Cl_2]$
b. $[HCl] = 2[H_2]$
c. $[HCl] = [H_2] = [Cl_2] = 1$
d. $[H_2][Cl_2]/[HCl]^2 = 1$

Question 9

For the reaction: A + B ⟷ C + D
6.0 moles of A and 5.0 moles of B are mixed together in a suitable container. When equilibrium

is reached, 4.0 moles of C are produced.
The equilibrium constant for this reaction is:
a. K = 1/8
b. K = 8
c. K = 30/16
d. K = 16/30

Question 10

The reaction is
N_2 (g) + 3 H_2 (g) $\leftrightarrow$ 2 NH_3 (g)
If hydrogen gas is added after the reaction has reached equilibrium, the reaction will:
a. shift to the right to produce more product
b. shift to the left to produce more reactants
c. stop. All the nitrogen gas has already been used up.
d. Need more information.

Answers

1. b. there are more products than reactants at equilibrium
2. b. K is greater than 1
3. a. $K = [HI]^2/[H_2][I_2]$
4. c. $K = [SO_3]^2/[SO_2]^2[O_2]$
5. d. $K = [CO_2]_2[H_2O]$
6. a. $K = [H_2O]^2/[H_2]^2$
7. c. 25
8. d. $[H_2][Cl_2]/[HCl]^2 = 1$
9. b. K = 8
10. a. shift to the right to produce more product

Name	Units	Symbol
molarity	$\frac{\text{moles solute}}{\text{liters solution}}$	M
formality	$\frac{\text{moles solute}}{\text{liters solution}}$	F
normality	$\frac{\text{equivalents solute}}{\text{liters solution}}$	N
molality	$\frac{\text{moles solute}}{\text{kilograms solvent}}$	m
weight percent	$\frac{\text{grams solute}}{\text{100 grams solution}}$	% w/w
volume percent	$\frac{\text{mL solute}}{\text{100 mL solution}}$	% v/v