

6.12. Calculate the concentrations of H_3O^+ , HOAc , and OAc^- , and OH^- in a solution that is prepared from 0.150 mole of HCl , 0.100 mole HOAc , and enough water to make 1.000 liter of solution. The dissociation constant for HOAc is 1.85×10^{-5} , and HCl is totally dissociated in aqueous solution.

6.14. To 1 liter of a solution containing 0.150 M NH_4Cl there is added 0.200 mole of solid NaOH . What are the ionic and molecular species that are in major concentration when equilibrium is reached? Calculate the concentrations of NH_3 , OH^- , and NH_4^+ at equilibrium if the dissociation constant for ammonia is 1.8×10^{-5} .

6.21. A solution is prepared by dissolving 0.200 mole of sodium formate, HCO_2Na , and 0.250 moles of formic acid, HCO_2H , in approximately 200 (± 50) ml of water. Calculate the concentrations of H_3O^+ and OH^- . The dissociation constant of formic acid is 1.8×10^{-4} .

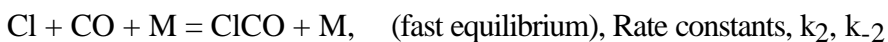
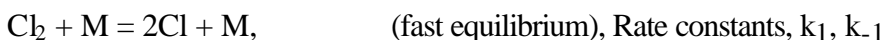
6.23. A solution of an unknown acid was titrated with base and the equivalence point reached when 36.12 ml of 0.100 M NaOH had been added. Then 18.06 ml of 0.100 M HCl were added to the solution and the measured pH was found with a pH meter to be 4.92. Calculate the dissociation constant of the unknown acid.

6.29. A solution is prepared by adding 2.05 gm of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, to 100 ml of 0.100 M HCl solution. What is the resulting concentration of H_3O^+ ? A subsequent addition of 6.00 ml of 0.100 M HCl is made. What is the new concentration of H_3O^+ ?

9.5. The reaction between carbon monoxide and chlorine to form phosgene ($\text{C}_2\text{Cl}_2\text{O}$), has the rate law



Show that the following mechanism is consistent with this rate law:



9.8. The following data give the concentration of gaseous butadiene as a function of time at 500°K. Plot them as $\ln c$ vs. t and as $1/c$ vs. t . Determine the order of the reaction, and calculate the rate constant.

$t(\text{sec})$	$C(\text{moles/liter})$	$t(\text{sec})$	$C(\text{moles/liter})$
195	1.62×10^{-2}	4140	0.89×10^{-2}
604	1.47×10^{-2}	4655	0.80×10^{-2}
1246	1.29×10^{-2}	6210	0.68×10^{-2}
2180	1.10×10^{-2}	8135	0.57×10^{-2}

9.11. It is often stated that near room temperature, a reaction rate doubles if the temperature increases by 10° . Calculate the activation energy of a reaction that obeys this rule exactly. Would you expect to find this rule violated frequently?

9.13. An electronically excited atom can either fluoresce or lose energy by collision with some other molecule. For example,

$\text{Hg}^* \rightarrow \text{Hg} + h\nu$, Rate constant k_1

$\text{Hg}^* + \text{Ar} \rightarrow \text{Hg} + \text{Ar}$, Rate constant k_2

These reactions are elementary processes. What is the rate law of each? What is the expression for the fraction of atoms lost by fluorescence at a given pressure of Ar?

17.25. For the reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, a run with $[\text{A}]_0 = 400 \text{ mmol dm}^{-3}$ and $[\text{B}]_0 = 0.400 \text{ mmol dm}^{-3}$ gave the following data (where $c^\circ \equiv 1 \text{ mol/dm}^3$):

$10^{-3}t/\text{s}$	0	120	240	360	infinity
$10^4[\text{C}]/c^\circ$	0	2.00	3.00	3.50	4.00

and a run with $[\text{A}]_0 = 0.400 \text{ mmol dm}^{-3}$ and $[\text{B}]_0 = 1000 \text{ mmol dm}^{-3}$ gave

$10^{-3}t/\text{s}$	0	69	208	485	infinity
$10^4[\text{C}]/c^\circ$	0	2.00	3.00	3.50	4.00

Find the rate law and the rate constant. The numbers have been chosen to make determination of the orders simple.

17.43. For the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, values of k are 1.2×10^{-3} and $3.0 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 700 and 629 K, respectively. Estimate E_a and A .

17.58. For the unimolecular isomerization of cyclopropane to propylene, values of k_{uni} vs. initial pressure of cyclopropane, P_0 , at 470°C are:

P_0/torr	110	211	388	760
$10^5 k_{\text{uni}}/\text{s}^{-1}$	9.58	10.4	10.8	11.1

Using $dP/dt = k_{\text{uni}} [A]$, where k_{uni} is derived from the Lindemann unimolecular reaction model, plot these data in a way that gives a straight line. From the slope and intercept, evaluate k_{uni} , at $P = \text{infinity}$ and the Lindemann parameters k_1 and k_{-1}/k_2 .