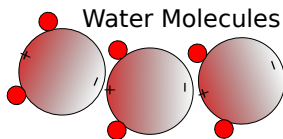


Water Properties

Water is a polar compound.

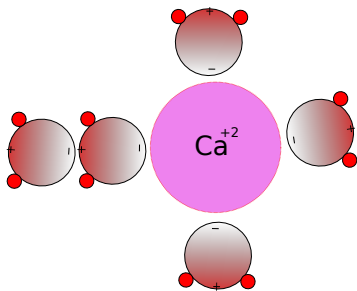
- ▶ liquid water molecules form chains
- ▶ solid water (ice): chains break, water expands.
- ▶ solid phase less dense than liquid phase.
- ▶ high surface tension



Water Properties

Water is a polar compound.

- ▶ effective solvent for ionic materials
- ▶ non-polar/uncharged substances sparingly soluble in water



Units of Measurement

- ▶ chemical mass per solution mass
 - ▶ ppm,ppb
 - ▶ mg per Kg, μg per Kg
- ▶ substance mass per solution volume
- ▶ molarity, moles per liter
- ▶ molality, moles per Kg solution
- ▶ equivalents (moles of charge)

Unit Conversion

27 ppm Ca^{2+} : convert to molality and equivalents per liter

$$\frac{27 \text{ mg } \text{Ca}^{2+}}{\text{Kg}} \left(\frac{1 \text{ mole}}{40080 \text{ mg}} \right) = 6.7 \cdot 10^{-4} \frac{\text{mole}}{\text{Kg}}$$

convert to molarity

$$6.7 \cdot 10^{-4} \frac{\text{mole}}{\text{Kg}} \left(\frac{1 \text{ Kg Water}}{\text{liter}} \right) = 6.7 \cdot 10^{-4} \frac{\text{mole}}{\text{liter}}$$

convert to equivalents

$$6.7 \cdot 10^{-4} \frac{\text{Mole}}{\text{liter}} \left(\frac{2 \text{ moles of charge}}{\text{mole of } \text{Ca}^{2+}} \right) = 1.34 \cdot 10^{-3} \frac{\text{eqv}}{\text{liter}}$$

Water Chemistry Parameters

- ▶ Bulk Water Chemistry
 - ▶ Total Dissolved Solids (mass of residue after evaporation per mass of solutions)
 - ▶ Specific Conductance (electrical conductivity of solution)
- ▶ Master Variables
 - ▶ pH ($-\log_{10}\{H^+\}$)
 - ▶ pe or Eh ($-\log_{10}\{e^-\}$)

$$Eh = \frac{n \cdot F \cdot pe}{2.3 \cdot R \cdot T} \approx .059pe(\text{at } 25 \text{ C})$$

- ▶ Acid neutralizing capacity (or Alkalinity)
- ▶ Hardness

Assessing Chemical Analysis

- ▶ Most natural waters dominated by 7 ions
 - ▶ Na^+ , Ca^{+2} , K^+ , Mg^{+2} , Cl^- , $HCO_3^- + CO_3^{-2}$, SO_4^{-2}
- ▶ Other important ions
 - ▶ $Fe^{+2,+3}$, SiO_4^{-4} , NO_3^- , NH_4^+ , BO_3^{-3} , PO_4^{-3} , Sr^{+2} , Mn
 - ▶ organic acids
- ▶ electroneutrality
- ▶ need filtered water sample

$$\%Err = \frac{\sum cations - \sum anions}{\sum cations + \sum anions}$$

$$\frac{\sum cations}{\sum anions} = Error Ratio$$

Acid Neutralizing Capacity

Ability of solution to buffer change in pH due to addition of acid

$$ANC = \sum (\text{base cations}) - \sum (\text{acid anions})$$

$$ANC \approx [HCO_3^-] + 2[CO_3^{2-}]$$

Other important species include organic acids, borate, ammonia, and sulfide.

Chemical Reactions

Types of Reactions

- ▶ dissolution/precipitation
- ▶ reduction/oxidation
- ▶ complexation
- ▶ surface reactions
 - ▶ ion exchange
 - ▶ adsorption
 - ▶ surface complexation
- ▶ Mixing

Assessing Data

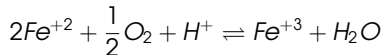
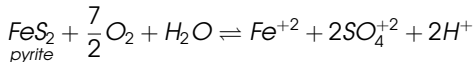
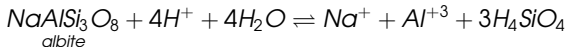
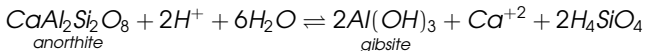
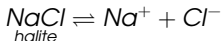
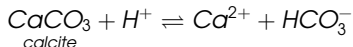
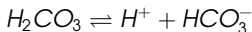
- ▶ Graphical
- ▶ Statistics
- ▶ Equilibrium
- ▶ Kinetics

Typical Concentrations and sources

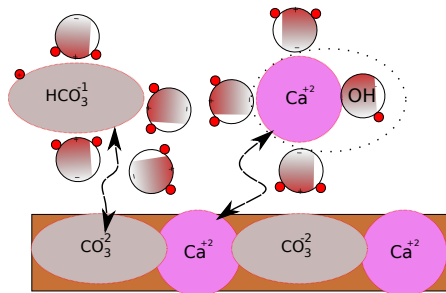
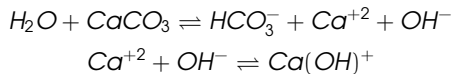
element	Conc(mmol/l)	potential source
Ca	0.05-5.	carbonate,gypsum, feldspar, pyroxene, amphibole
Na	0.01-0.2	feldspar,halite,zeolite,atmosphere
K	0.01-0.2	feldspar,mica
Mg	0.05-2	dolomite,serpentine,pyroxene,amphibole,mica
Cl	0.05-2	salts, atmosphere
HCO ₃	0.-5.	organics,carbonate, atmosphere
SO ₄	0.01-5	gypsum,sulfides,atmosphere

(Appelo and Postma,1996)

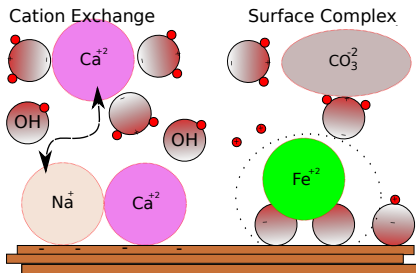
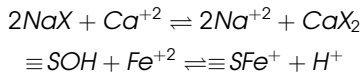
Common Natural Geochemical Reactions



Dissolution and Complexation



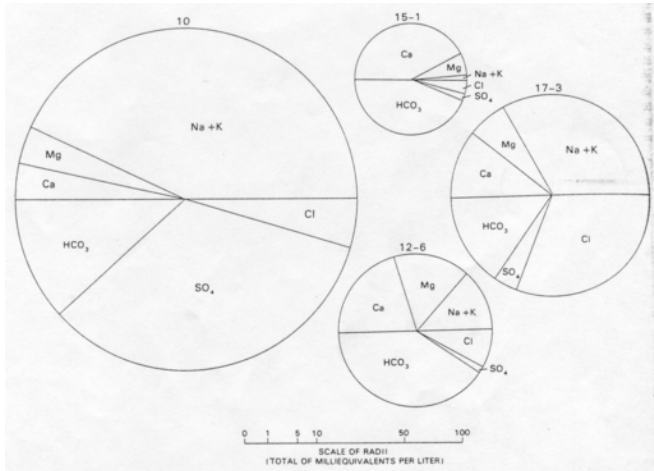
Surface Processes



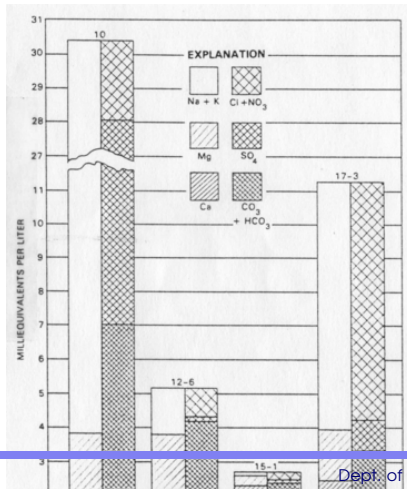
Graphical Display-Standard Methods

- ▶ Univariate
 - ▶ histograms
 - ▶ box and whisker
- ▶ multivariate
 - ▶ pie charts
 - ▶ bar charts
 - ▶ scatter plots
- ▶ spatial

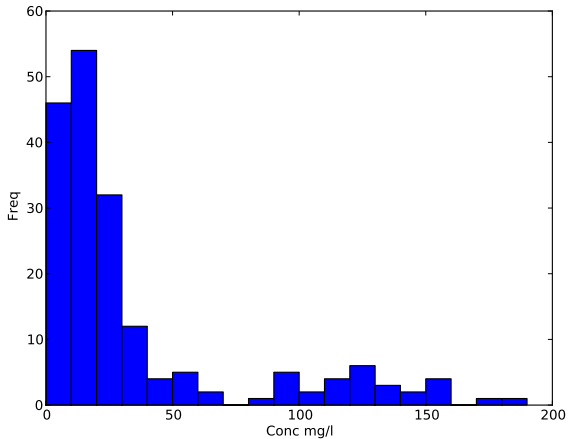
Pie Chart



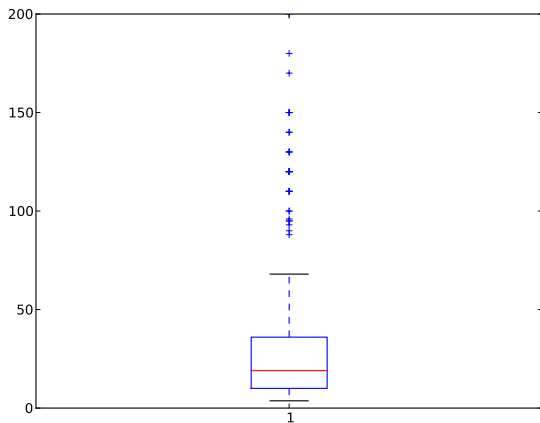
Bar Chart



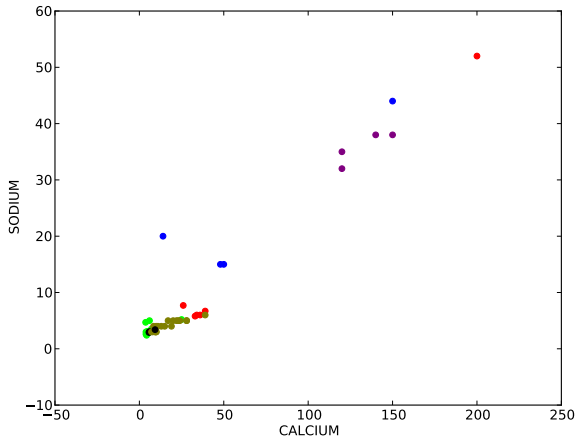
Histogram (Ca)



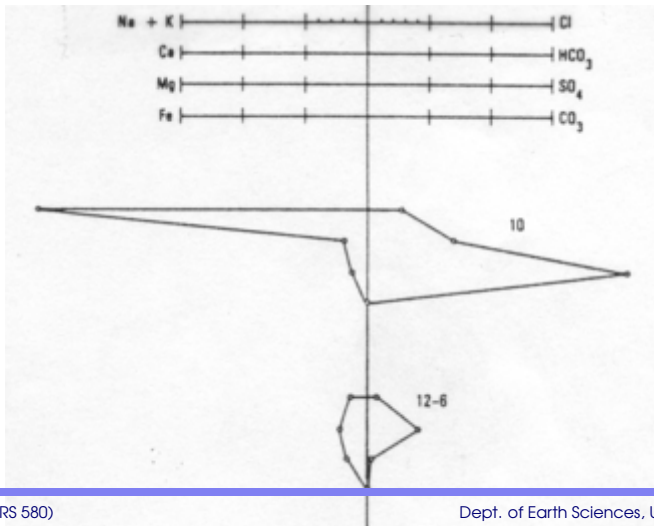
Box and Whisker (Ca)



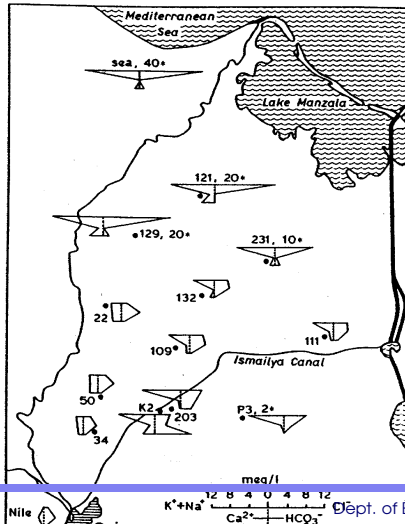
Scatter plot (Ca vs. Na)



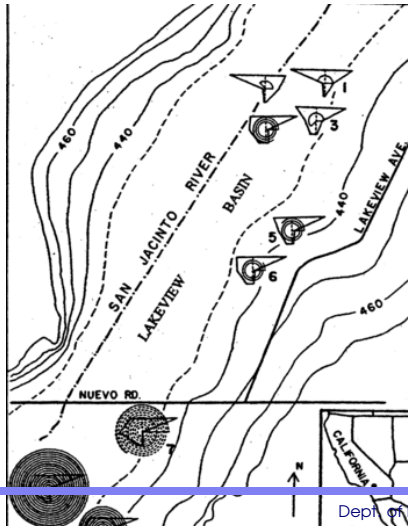
Stiff Plot



Stiff Plot

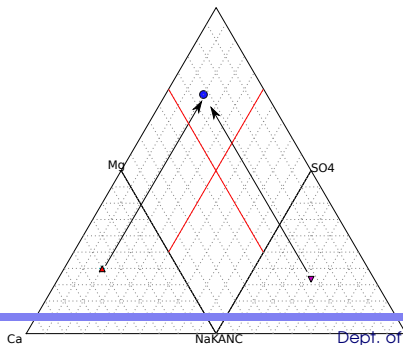


Stiff Plot

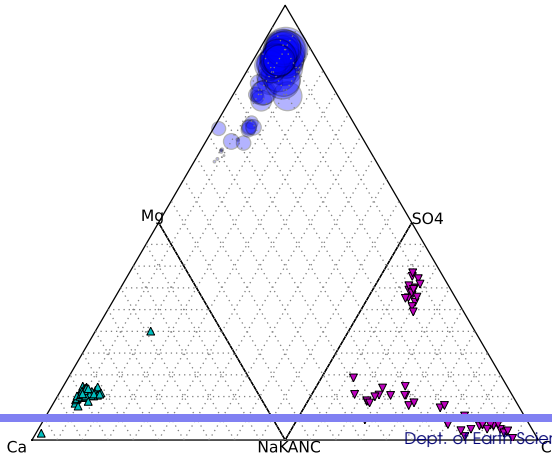


Piper Plot

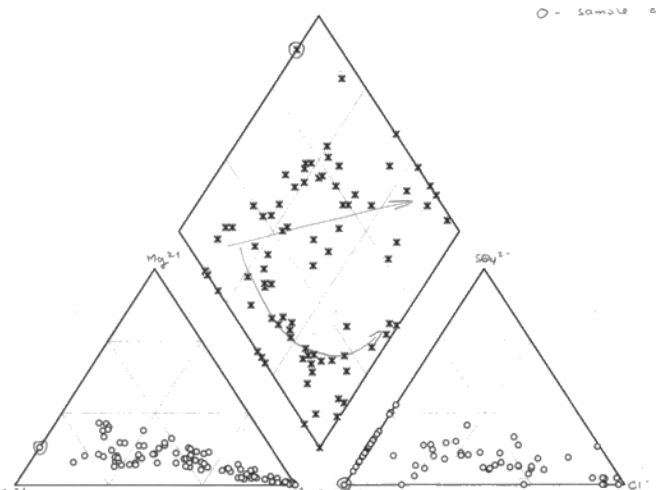
- ▶ Data converted to % equivalents (closed data sets)
- ▶ Projecting from cation and anion fields
- ▶ Classifying water types



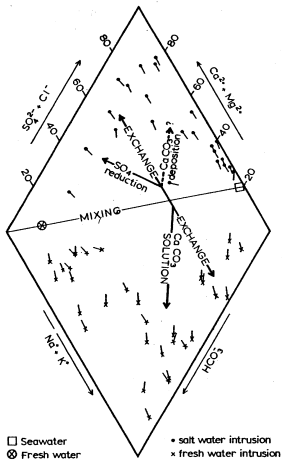
Piper Plot(Landfill)



Piper Plot (Domestic Maine Wells)



Piper Plot (Piper Process Pathways)



Equilibrium Calculations

- ▶ A solution is a phase that contains a variety of species.
- ▶ A phase is physically distinct, homogeneous region.
- ▶ Surfaces separate different phases
 - ▶ surfaces create abrupt changes in material properties
 - ▶ Different phases can be mechanically separated

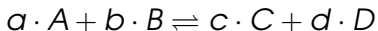
- ▶ Different species are contained within a solution.
- ▶ Species characterized by:
 - ▶ chemical formula and molecular structure
 - ▶ phase it occurs in
- ▶ Species are not the fundamental variable for formal equilibrium calculations
- ▶ Components
 - ▶ subset of species
 - ▶ can create all species from components

Tableau

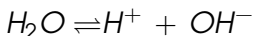
	Ca^{2+}	OH^{-}	H_2O
Ca^{2+}	1		
OH^{-}		1	
H_2O			1
H^{+}		-1	1
$CaOH^{+}$	1	1	
$Ca(OH)_2^0$	1	2	

Law of Mass Action

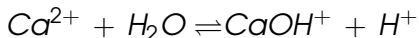
- ▶ The law of mass action links species and components.
- ▶ Each line in tableau represents a chemical reaction.



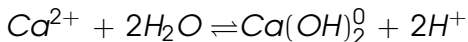
$$K_{eq} = \frac{C^c \cdot D^d}{A^a \cdot B^b}$$



$$K_{eq} = 10^{-14}$$



$$K_{eq} = 10^{-12.78}$$



$$K_{eq} = 10^{-22.8}$$

Activity

- ▶ the activity of species must be determined.
- ▶ empirical relationships between the concentration and activity
- ▶ activity coefficient (γ) applicable to relatively dilute systems

$$a_i = \gamma_i \cdot m_i$$

- ▶ accounts for the non-ideal behavior of solutes.

Activity

- ▶ The electrical interaction between solutes interferes with the chemical reactions in a solution, lowering the effective concentration of ions in solution.
- ▶ As the ionic strength of a solution approaches zero, the activity of a species will approach its concentration.
- ▶ The Debye-Huckel theory is based on the idea that the electrical (Coulombic) interaction decreases with the inverse of distance.

$$I = \frac{1}{2} \sum m \cdot z^2$$

Debye-Huckel model accurate to $I=0.01$, A is about 0.5 at 25° C, and varies with temp.

$$\log(\gamma_i) = -Az^2\sqrt{I}$$

Extended Debye-Huckel model accurate to about $I=0.1$, a is dependent on ion, B is about 0.33 and varies with temp.

$$\log(\gamma_i) = -\frac{Az^2\sqrt{I}}{1 + a_iB\sqrt{I}}$$

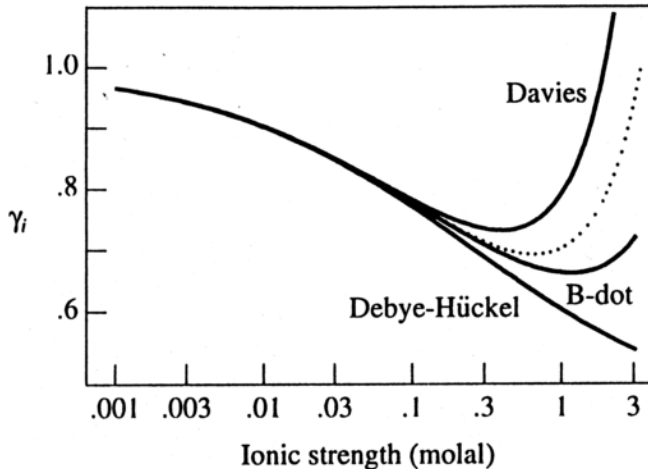
Davies model accurate to $I=0.3$, coefficient (0.3) can vary

$$\log(\gamma_i) = -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

B-dot model , \dot{B} is traditionally temp. dependent
this model was developed so activity could
be calculated at higher temp.
PHREEQC uses ion specific values for \dot{B}

$$\log(\gamma_i) = -\frac{Az^2\sqrt{I}}{1 + a_iB\sqrt{I}} + \dot{B}I$$

Activity Coef. Comparison



Saturation State

- ▶ Ion Activity Product (IAP, based on activities in sample)
- ▶ Equilibrium Constant (K_{eq} , based on activities at equilibrium)
- ▶ Saturation State ($\Omega = \frac{IAP}{K_{eq}}$)
- ▶ Saturation Index ($\log_{10} \left(\frac{IAP}{K_{eq}} \right)$)

Using Equilibrium Calculations

Question?

Is the following solution supersaturated w.r.t Calcite?

pH	8.27
ANC	$799 \mu\text{eq} \cdot \text{l}^{-1}$
Ca	$13.1 \text{ mg} \cdot \text{l}^{-1}$
Mg	$1.57 \text{ mg} \cdot \text{l}^{-1}$
K	$0.97 \text{ mg} \cdot \text{l}^{-1}$
Na	$4.28 \text{ mg} \cdot \text{l}^{-1}$
Cl	$55. \mu\text{eq} \cdot \text{l}^{-1}$
SO ₄	$152 \mu\text{eq} \cdot \text{l}^{-1}$
NO ₃	$2.9 \mu\text{eq} \cdot \text{l}^{-1}$

Using Equilibrium Calculations

Preliminary Steps

- ▶ Conversion
- ▶ Error Check

		GFW	charge	mmol/l	meq/l
pH	8.27				
ANC	799	1	1	0.799	0.799
Ca	13.1	40.08	2	0.327	0.654
Mg	1.57	24.31	2	0.065	0.129
K	0.97	39.1	1	0.025	0.025
Na	4.28	22.99	1	0.186	0.186
Cl	55	1	1	0.055	0.055
SO4	152	1	2	0.076	0.152
NO3	2.9	1	1	0.003	0.003
				sumCat	0.99
				SumAn	1.01
				% Error	-0.75%

Simple Method

- ▶ Assume ANC=HCO₃, no complexes
- ▶ Calculate ionic strength ($I = \frac{1}{2} \cdot \Sigma mz^2$)
- ▶ Calculate IAP
- ▶ Calculate Saturation Index

Simple Method

	mmol/l	charge	$.5 \cdot m \cdot z^2$
pH	8.27		
ANC	0.799	1	0.4
Ca	0.327	2	0.65
Mg	0.065	2	0.13
K	0.025	1	0.01
Na	0.186	1	0.09
Cl	0.055	1	0.03
SO4	0.076	2	0.15
NO3	0.003	1	0
		Ionic Strength(I)	$1.47 \cdot 10^{-3}$

Sample Calc: Saturation w.r.t Gypsum

$$\log(\gamma) = \frac{-A \cdot z^2 \sqrt{I}}{1 + B \cdot a_i \sqrt{I}}$$

- ▶ $A (\approx .5)$, $B (\approx .33)$, and a tabulated in textbook
- ▶ $a_{Ca} = 6$, $a_{HCO_3} = a_{SO_4} = 4$, $a_{CO_3} = 5$
- ▶ $\gamma_{Ca} = .84$, $\gamma_{CO_3} = .84$

Equilibrium saturation state calculations done in class

Chemical Kinetics

- ▶ Description of chemical reactions through rate laws
- ▶ Reactions are one way processes
- ▶ Proceeds based on order of the reaction and rate constant
- ▶ Equilibrium: a forward and reverse reaction at steady state

When to use chemical kinetics

- ▶ One way processes:
 - ▶ radioactive decay
 - ▶ organic decay
- ▶ Time constraint
 - ▶ transport: inadequate time to equilibrate with surroundings
 - ▶ track change in conc as approach equilibrium

Chemical Kinetics

breakdown of TCA to DCA:



First order reaction:

$$\frac{d[\text{TCA}]}{dt} = k[\text{TCA}]^1$$

Rate equation can involve more than one constituent.

$$\frac{d[Fe^{2+}]}{dt} = -k \cdot [Fe^{2+}] \cdot [OH^{-}]^2 \cdot P_{O_2}$$

The rate of iron oxidation is first order with respect to oxygen and iron, and second order with respect to hydroxide.

Simple Analytic Solutions

- ▶ Zeroth order:

$$\frac{dC}{dt} = K$$
$$C = C_0 + K\Delta t$$

- ▶ First Order

$$\frac{dC}{dt} = KC$$
$$C = C_0 e^{(K \cdot \Delta t)}$$

Kinetic Plots

