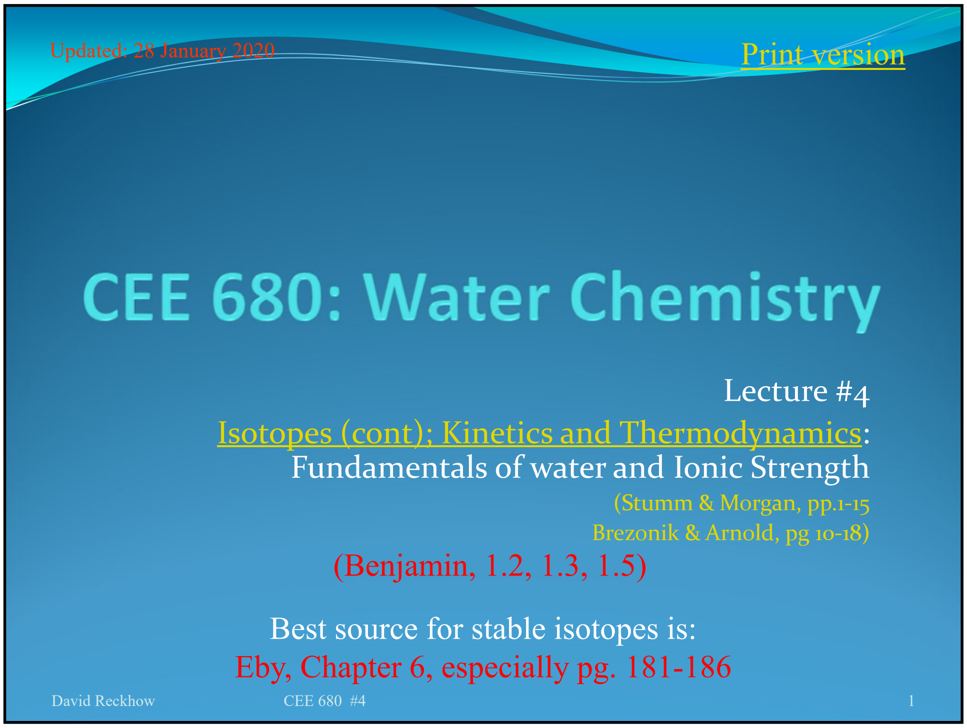


Updated: 28 January 2020

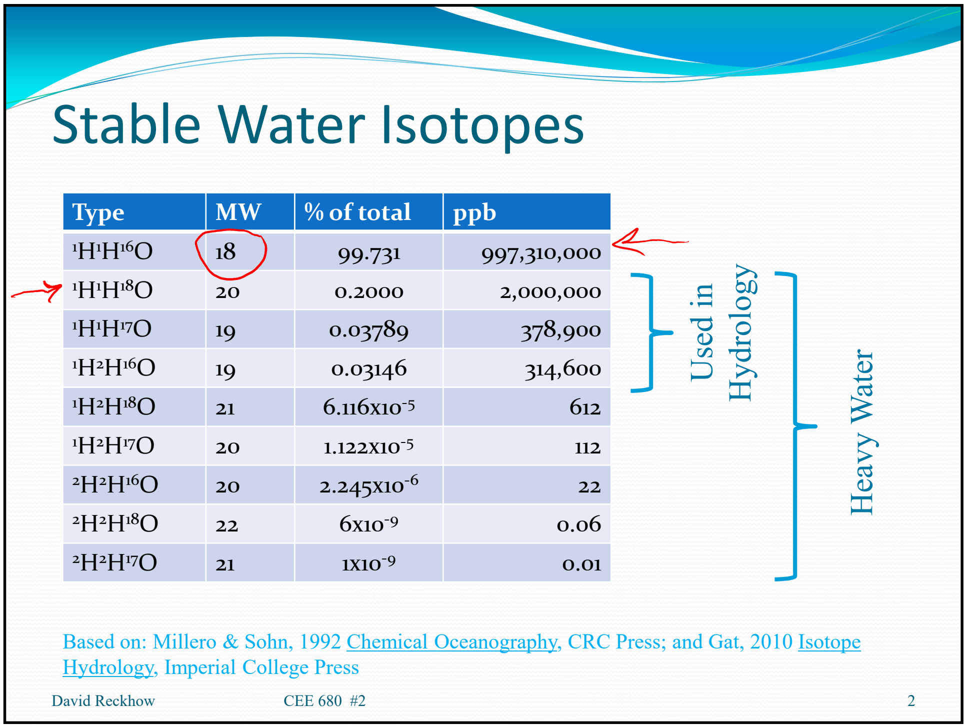
Print version

CEE 680: Water Chemistry

Lecture #4

Isotopes (cont); Kinetics and Thermodynamics:
Fundamentals of water and Ionic Strength
(Stumm & Morgan, pp.1-15
Brezonik & Arnold, pg 10-18)
(Benjamin, 1.2, 1.3, 1.5)

Best source for stable isotopes is:
Eby, Chapter 6, especially pg. 181-186



Stable Water Isotopes

Type	MW	% of total	ppb
$^{1}H^{1}H^{16}O$	18	99.731	997,310,000
$^{1}H^{1}H^{18}O$	20	0.2000	2,000,000
$^{1}H^{1}H^{17}O$	19	0.03789	378,900
$^{1}H^{2}H^{16}O$	19	0.03146	314,600
$^{1}H^{2}H^{18}O$	21	6.116×10^{-5}	612
$^{1}H^{2}H^{17}O$	20	1.122×10^{-5}	112
$^{2}H^{2}H^{16}O$	20	2.245×10^{-6}	22
$^{2}H^{2}H^{18}O$	22	6×10^{-9}	0.06
$^{2}H^{2}H^{17}O$	21	1×10^{-9}	0.01

Used in Hydrology

Heavy Water

Based on: Millero & Sohn, 1992 Chemical Oceanography, CRC Press; and Gat, 2010 Isotope Hydrology, Imperial College Press

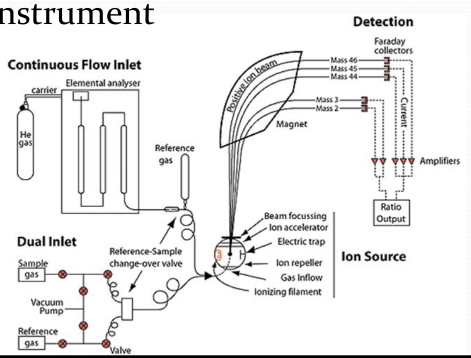
Properties of Stable Water Isotopes

Property	$^1H^1H^{16}O$	$^1H^1H^{18}O$	$^1H^2H^{16}O$	$^2H^2H^{16}O$	units
Density @30°C		1.107845	1.04945	1.10323	g/mL
Temp@ d_{max}		4.305		11.24	°C
Boiling Pt		100.14		101.42	°C
Melting Pt		0.28		3.81	°C
Diffusivity in water @25°C		2.66		2.34	10^3 cm^2s^{-1}
Relative diffusivity in air	1.0000	0.9723	0.9755		

From: Gat, 2010 Isotope Hydrology, Imperial College Press and references therein

Measurement

- Requires separation of H from O in water
  - Hydrogen goes to H2 with help of a hot metal catalyst
  - Oxygen goes to O2 by hydrolysis or fluorination or to CO2 by aqueous equilibration
- Then use an isotope ratio instrument
  - Magnetic sector Mass Spectrometer
  - Wavelength-Scanned Cavity Ring Down Spectrometer (WS-CRDS)



Relative Isotopic Abundance

- Reflects environmental fractionation
  - Helps describe origins, pathways, processes
  - Tracer
- Calculation based on a standard material
  - Uses ratios of abundance; eg:

$$\boxed{\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) x1000}$$

- Where: R is the isotopic ratio, e.g., for oxygen

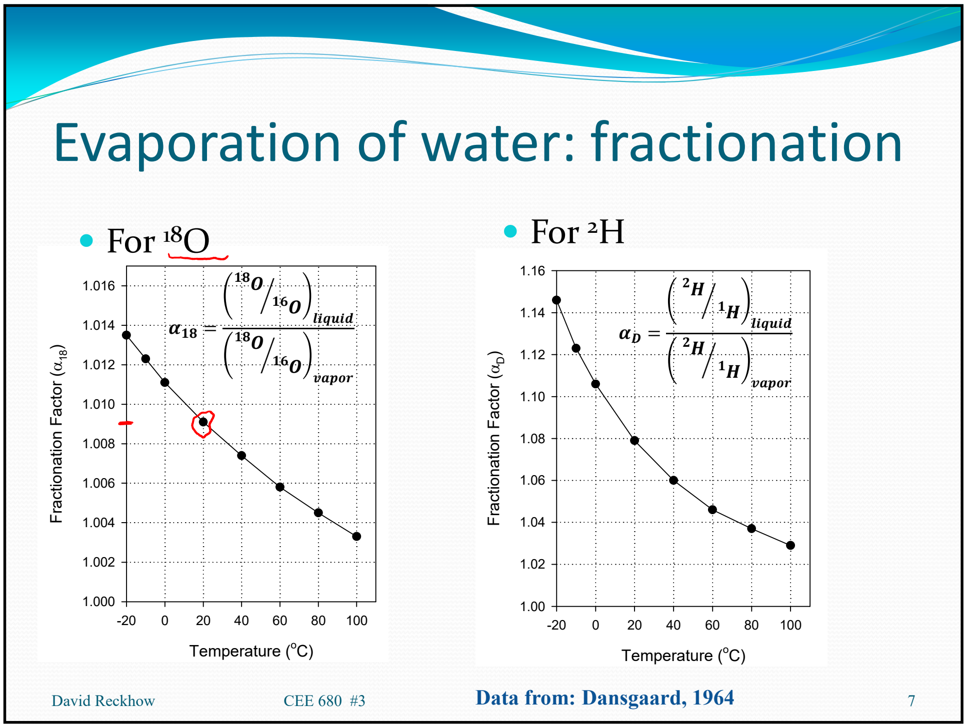
$$\boxed{R = {}^{[18}O]\big/ [{}^{16}O]}$$

Fundamentals of Isotope Geochemistry

Isotopic Standards in %

Ratio	Nominal	V-SMOW	PDB	
$^2H/^1H$	0.015	0.015576		
$^{13}C/^{12}C$	1.1		1.12375	
$^{18}O/^{16}O$	0.2	0.20052	0.20672	

- Key to Standards
  - V-SMOW = Vienna Standard Mean Ocean Water
    - established by IAEA in Vienna; blend of ocean waters around globe
  - PDB = PeeDee Belemnite (high $^{13}C/^{12}C$ ratio)
    - Fossilized cephalopods from the PeeDee River in SC



Evaporation of water: fractionation

- For $^{18}\underline{O}$
- For ^{2}H

$$\alpha_{18} = \frac{\left(^{18}O/^{16}O\right)_{liquid}}{\left(^{18}O/^{16}O\right)_{vapor}}$$

$$\alpha_D = \frac{\left(^{2}H/^{1}H\right)_{liquid}}{\left(^{2}H/^{1}H\right)_{vapor}}$$

Data from: Dansgaard, 1964

example

- A rainwater sample from Boston has an $^{18}O/^{16}O$ ratio of 0.0019750 as determined by isotope ratio MS.
  1. Calculate the delta value vs V-SMOW (in ‰)

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) x1000 = \left(\frac{0.0019750 - 0.0020052}{0.0020052}\right) x1000 = \boxed{-15.1}$$

  2. Determine the delta value for the water vapor that is in equilibrium with at 20C

R_L

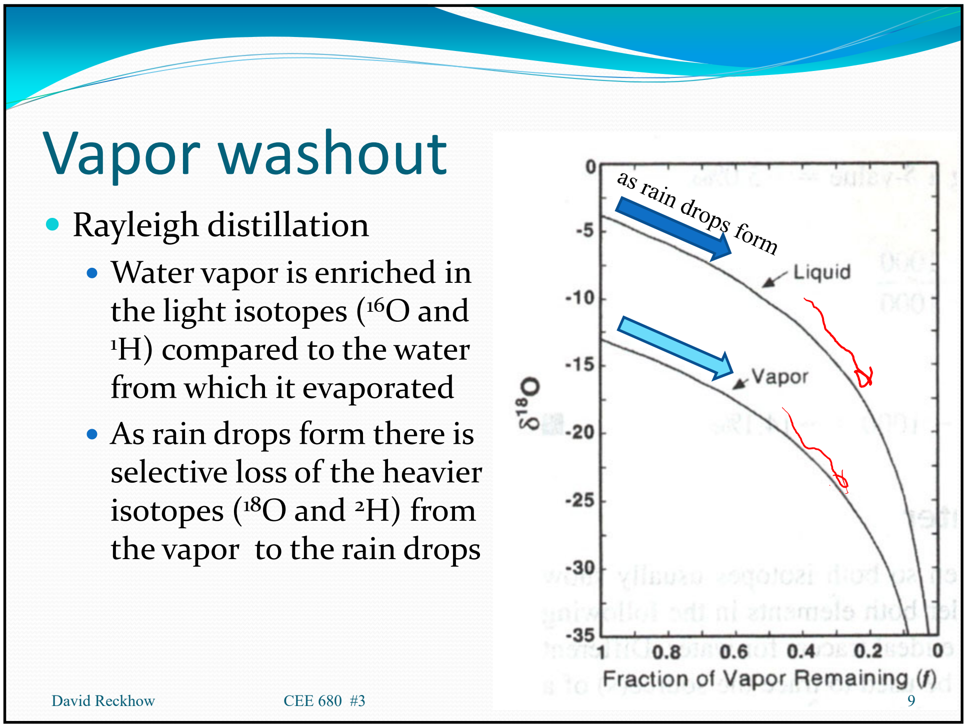
$$\alpha_{18} = \frac{\left(^{18}O/^{16}O\right)_{liquid}}{\left(^{18}O/^{16}O\right)_{vapor}} = \underline{1.009}$$

R_V

$$\alpha_{18} = \frac{0.0019750}{R_{vapor}} = 1.009$$

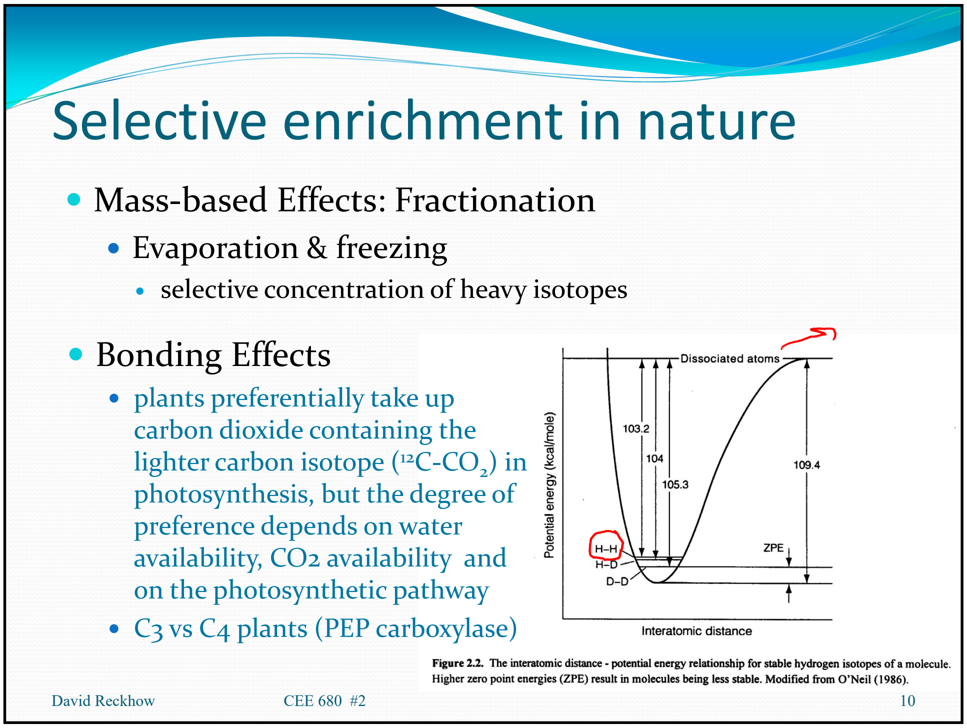
$$R_{vapor} = 0.0019574$$

$$\delta = \left(\frac{0.0019750 - 0.0020052}{0.0020052}\right) x1000 = -23.8$$



Vapor washout

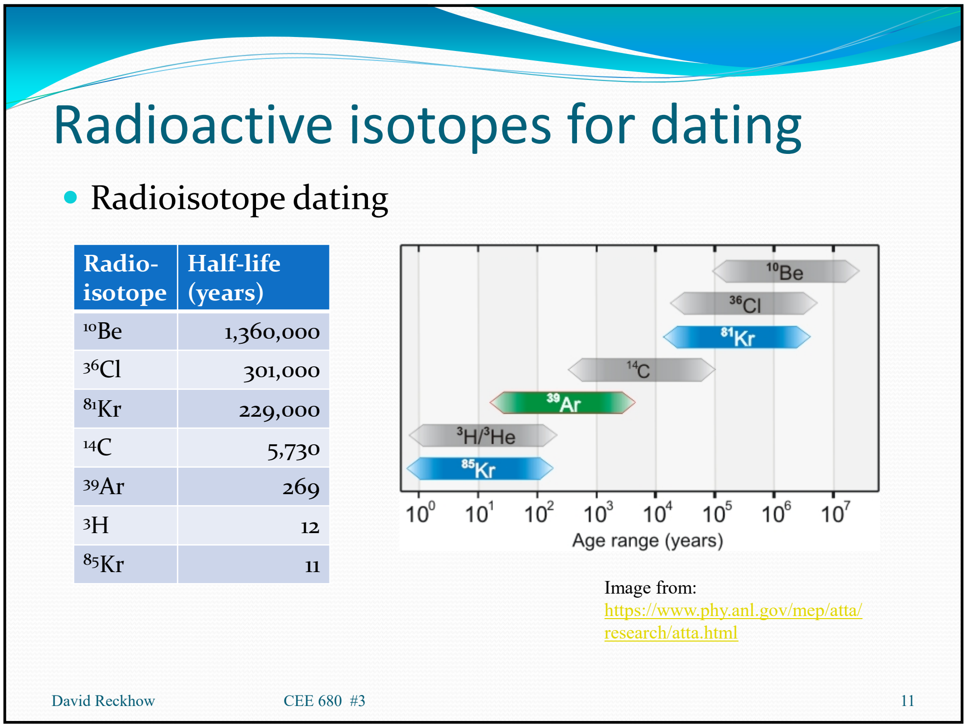
- Rayleigh distillation
  - Water vapor is enriched in the light isotopes (^{16}O and ^{1}H) compared to the water from which it evaporated
  - As rain drops form there is selective loss of the heavier isotopes (^{18}O and ^{2}H) from the vapor to the rain drops



Selective enrichment in nature

- Mass-based Effects: Fractionation
  - Evaporation & freezing
    - selective concentration of heavy isotopes
- Bonding Effects
  - plants preferentially take up carbon dioxide containing the lighter carbon isotope (^{12}C-CO_2) in photosynthesis, but the degree of preference depends on water availability, CO2 availability and on the photosynthetic pathway
  - C3 vs C4 plants (PEP carboxylase)

Figure 2.2. The interatomic distance - potential energy relationship for stable hydrogen isotopes of a molecule. Higher zero point energies (ZPE) result in molecules being less stable. Modified from O'Neil (1986).

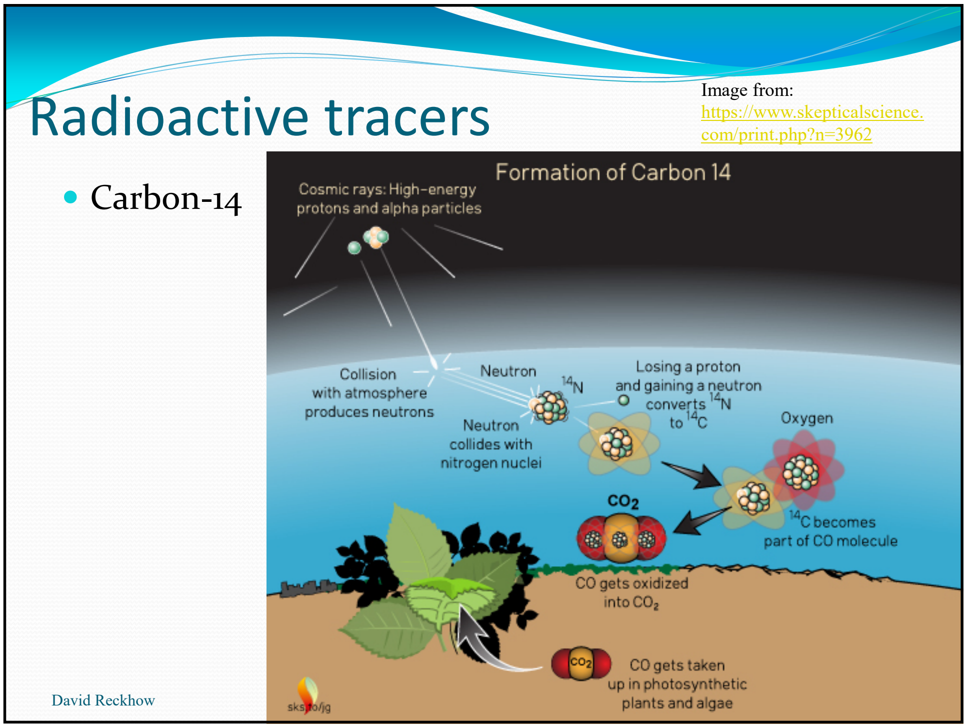


Radioactive isotopes for dating

- Radioisotope dating

Radio-isotope	Half-life (years)
^{10}Be	1,360,000
^{36}Cl	301,000
^{81}Kr	229,000
^{14}C	5,730
^{39}Ar	269
^{3}H	12
^{85}Kr	11

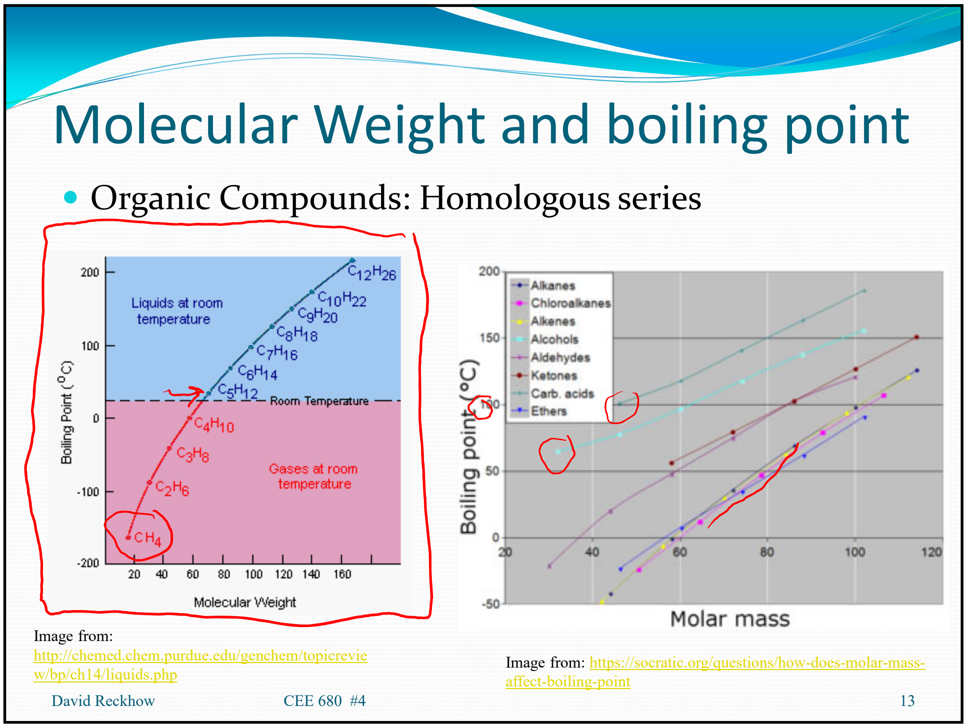
Image from: https://www.phy.anl.gov/mep/atta/research/atta.html



Radioactive tracers

Image from: https://www.skepticalscience.com/print.php?n=3962

- Carbon-14



Molecular Weight and boiling point

- Organic Compounds: Homologous series

Image from: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch14/liquids.php

Image from: https://socratic.org/questions/how-does-molar-mass-affect-boiling-point

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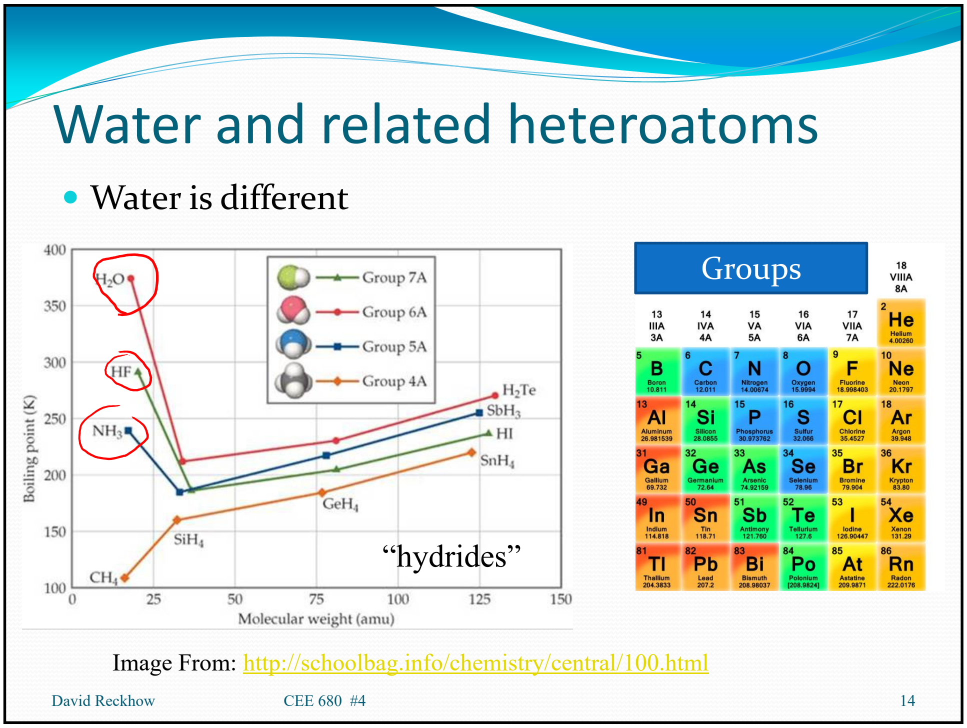

Water and related heteroatoms

- Water is different

"hydrides"

Image From: http://schoolbag.info/chemistry/central/100.html

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Water is exceptional

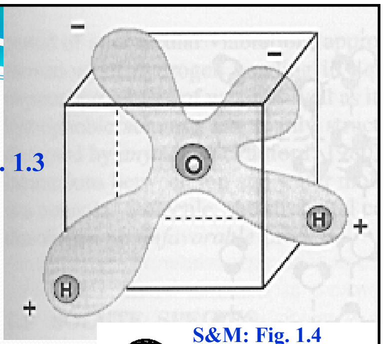
- From Eby, 2016 (Table 1-7)

Property	Comparison to other substances
Heat capacity	Highest of all common liquids (except ammonia) and solids
Latent heat of fusion	Highest of all common liquids (except ammonia) and most solids
Latent heat of vaporization	Highest of all common substances
Dissolving ability	Dissolved more substances (particularly ionic compounds), and in greater quantity than any other common liquid
Transparency	Relatively high for visible light
Physical state	The only substance that occurs naturally in all three states at the earth's surface
Surface tension	Highest of all common liquids
Conduction of heat	Highest of all common liquids (Hg is higher)
Viscosity	Relatively low viscosity for a liquid

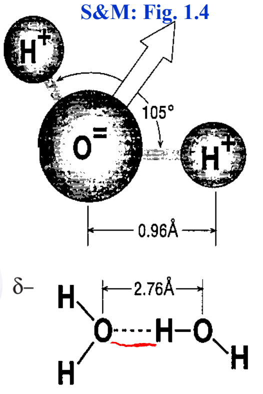
Structure of Water

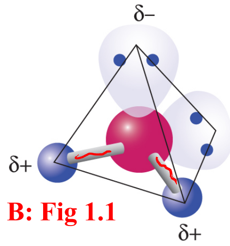
- sp³ hybridization
  - 2 bonding and 2 non-bonding orbitals
- Dipolar Character
- Origin of Water's Unusual properties
  - High melting and boiling point
  - High heat of vaporization
  - Expands upon freezing
  - High surface tension
  - Excellent polar solvent

S&M: Fig. 1.3

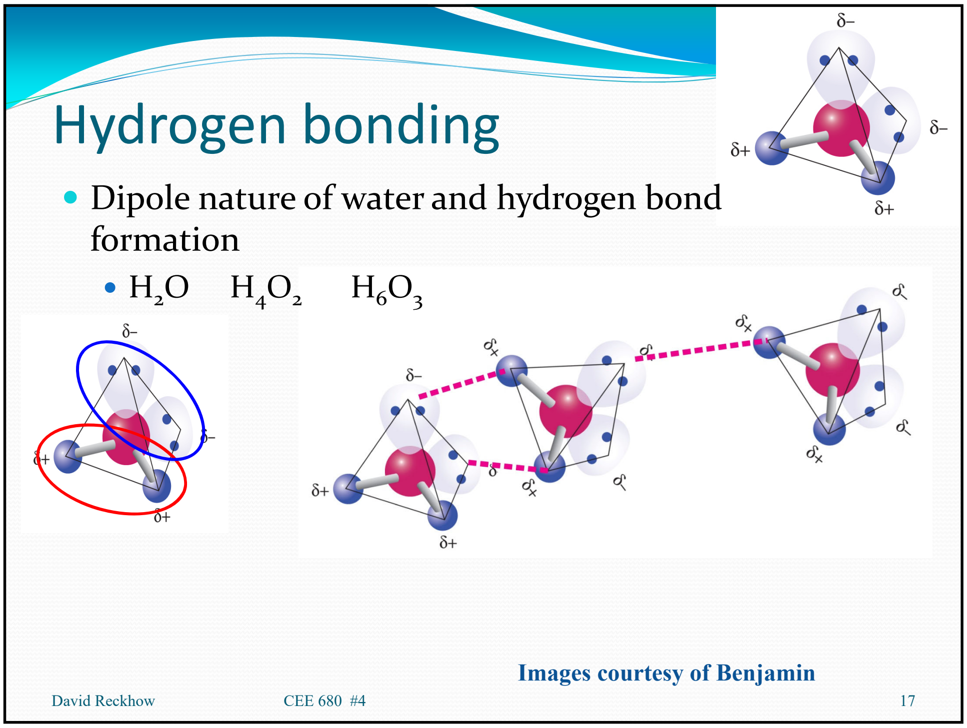


S&M: Fig. 1.4





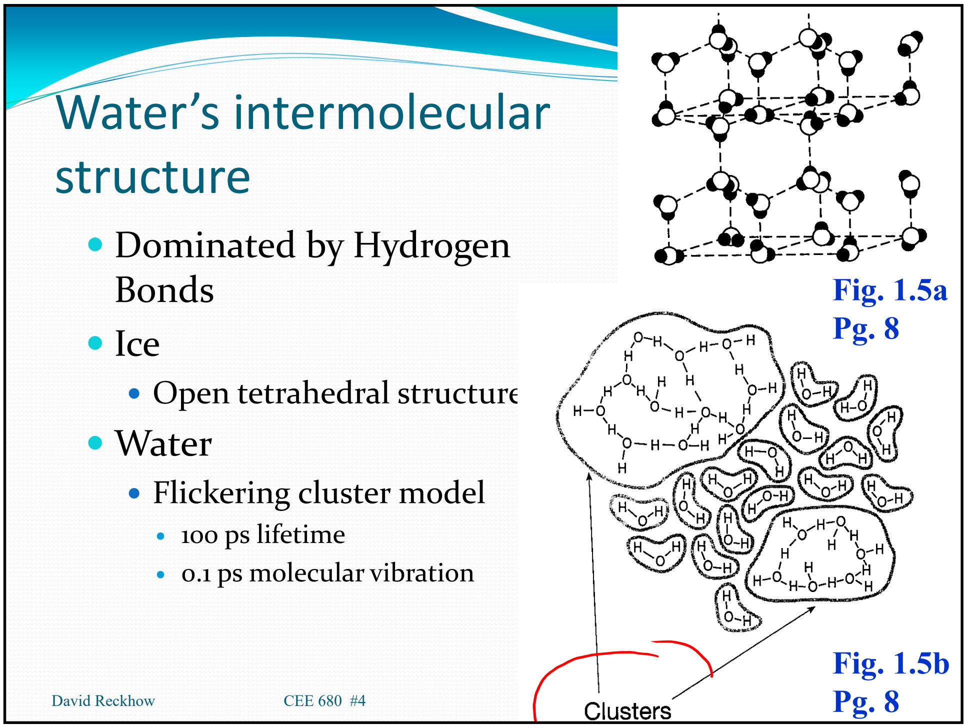
B: Fig 1.1



Hydrogen bonding

- Dipole nature of water and hydrogen bond formation
  - H_2O H_4O_2 H_6O_3

Images courtesy of Benjamin



Water's intermolecular structure

- Dominated by Hydrogen Bonds
- Ice
  - Open tetrahedral structure
- Water
  - Flickering cluster model
    - 100 ps lifetime
    - 0.1 ps molecular vibration

Fig. 1.5a
Pg. 8

Fig. 1.5b
Pg. 8

Freezing and density

- Crystalline structure
  - Lower density than liquid water
- Max density is at 4°C

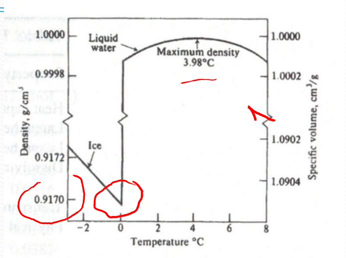
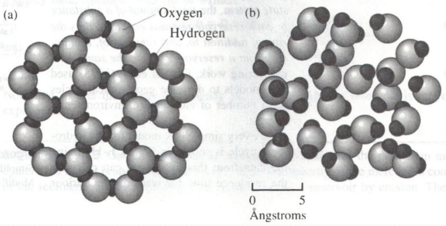


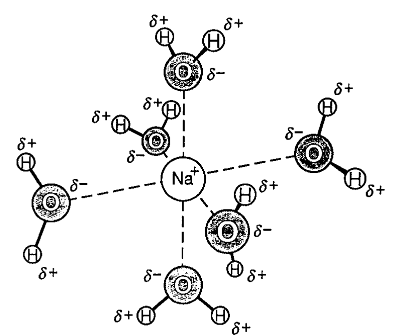
Figure 1–9
Density of pure water near the freezing point. From Duxbury (1971).

Figure 1–8
(a) The crystal structure of ice showing the six-sided rings formed by 24 water molecules. (b) The structure of liquid water. In the same volume of liquid water, there are 27 water molecules; hence, liquid water has a greater density than ice. From Gross and Gross (1996).



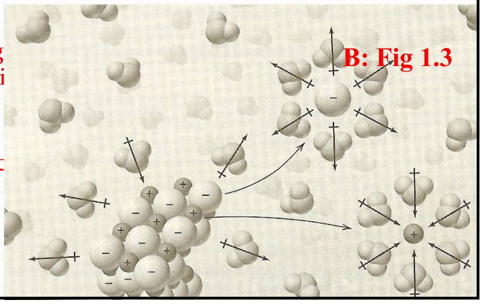
Images from Eby, 2016

Solutes in Water

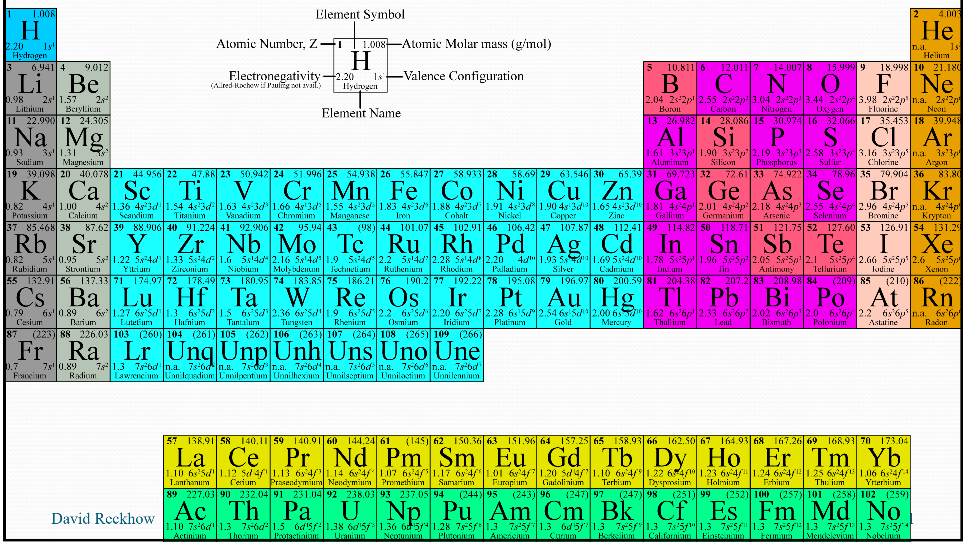


S&M: Fig. 1.6

- Great solvent for ionic or ionizable substances
- Ion-dipole bonds improves stability
  - Energy increases with charge of ion and decreases with size
  - Solvent hole model
    - As solute-water bonding streng compared to water-water bondi solubility goes up
      - Hydrophilic solute
    - Weak solute-water bonds reduc solubility
      - Hydrophobic solutes


B: Fig 1.3

Periodic Table



"680 Periodic Table"

H 4.5 H_2O -1.74 -1.74							**He** 8.8
Li 6.3 Li^+ 4.6	**Be** $BeOH^+$ (?) 9.2	**B** 7.0 H_3BO_4 3.39	**C** 4.9 HCO_3^- 2.64 3.0	**N** 6.3 N_2, NO_3^- 1.97	**O** 4.5 H_2O, O_2 -1.74 -1.74	**F** 5.7 F^-, MgF^+ 4.17 5.3	**Ne** 8.15
Na 7.7 Na^+ 0.33 3.57	**Mg** 7 Mg^{+2}, $MgSO_4$ 1.27 3.77	**Al** 2 $Al(OH)_4^-$ 7.1	**Si** 3.8 H_4SiO_4 4.15 3.8	**P** 4 HPO_4^{-2} 5.3	**S** 6.9 SO_4^{-2}, $NaSO_4^-$ 1.55 3.92	**Cl** 7.9 Cl^- 0.26 3.66	**Ar** 6.96
K 6.7 K^+ 1.99 4.23	**Ca** 5.9 Ca^{+2}, $CaSO_4$ 1.99 3.42			**As** $HAsO_4^{-2}$ 7.3	**Se** 4 SeO_3^{-2} 8.6	**Br** 8 Br^- 3.08	**Kr** 8.6
	Sr 6.6 Sr^{+2} 4.05					**I** 6 I^-, IO_3^- 6.3	
	Ba 4.5 Ba^{+2} 6.8						

- Ocean residence time (log yr)
- Predominant species
- River Water conc. (-log M)
- Seawater conc. (-log M)

After S&M:Fig. 1.7, Pg. 10

Law of Mass Action

- The rate of an elementary reaction is proportional to the product of the concentrations of the participating molecules, atoms or ions
- Chemical equilibria comes from the combination of two competing rates
  - Consider the autodecomposition of water

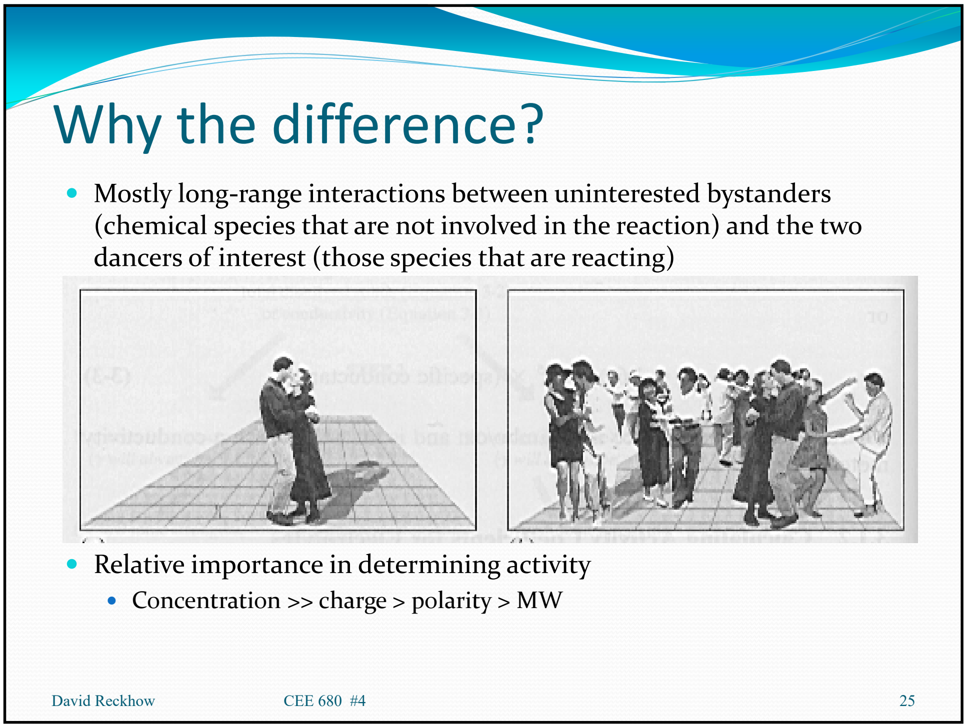
$$H_2O \leftrightarrow H^+ + OH^-$$

⇨ **Equilibrium Quotients**

- Other examples
  - acid dissociation, Precipitation, Redox, Adsorption, volatilization

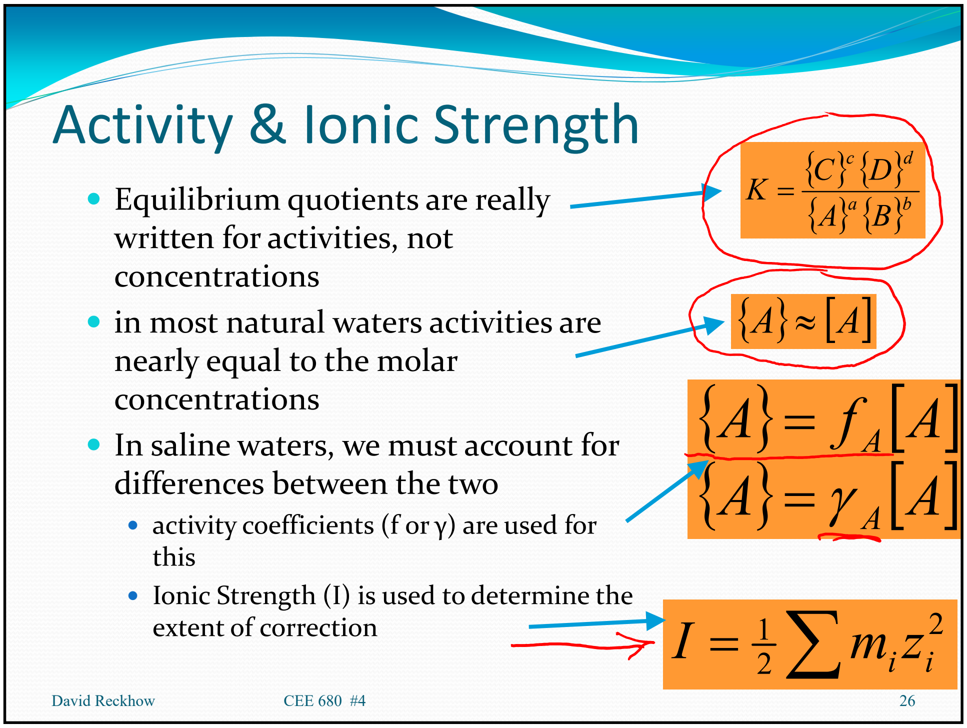
Activity

- Activity is the "effective" concentration or "reactivity", which may be slightly different from the true "analytical" concentration
  - These two differ substantially in waters with high TDS, such as sea water.
- We identify these two as follows:
  - Curved brackets ({X}) indicate activity
  - Square brackets ([X]) indicate concentration
    - Usually this is molar concentration
    - This may also be used when we're not very concerned about the differences between activity and concentration



Why the difference?

- Mostly long-range interactions between uninterested bystanders (chemical species that are not involved in the reaction) and the two dancers of interest (those species that are reacting)
- Relative importance in determining activity
  - Concentration >> charge > polarity > MW



Activity & Ionic Strength

- Equilibrium quotients are really written for activities, not concentrations
- in most natural waters activities are nearly equal to the molar concentrations
- In saline waters, we must account for differences between the two
  - activity coefficients (f or γ) are used for this
  - Ionic Strength (I) is used to determine the extent of correction

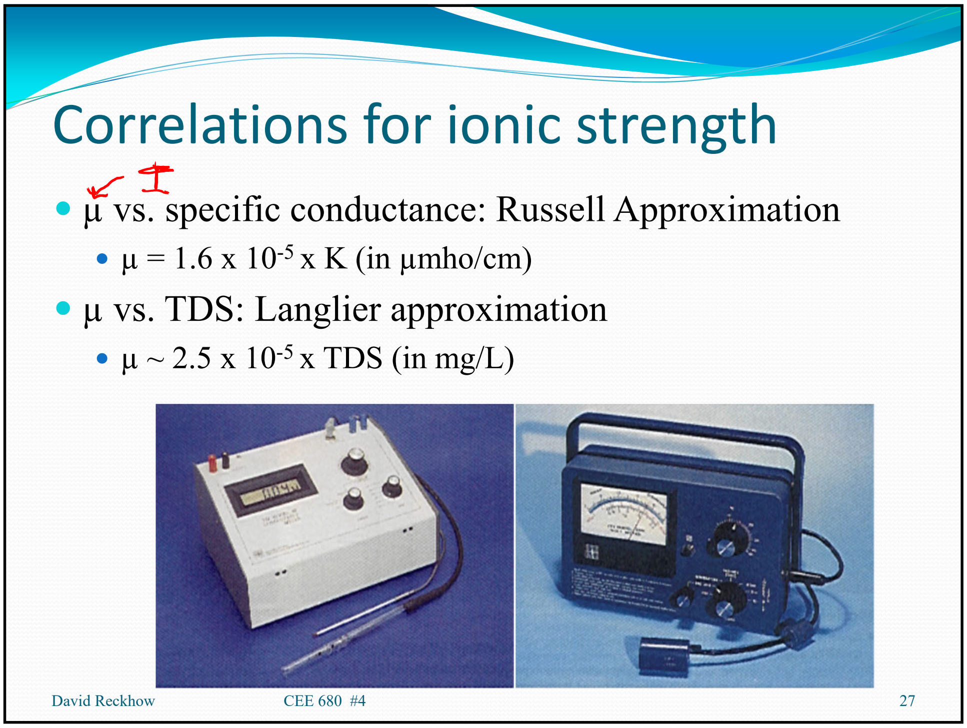
$$K = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$

$$\{A\} \approx [A]$$

$$\{A\} = f_A[A]$$

$$\{A\} = \gamma_A[A]$$

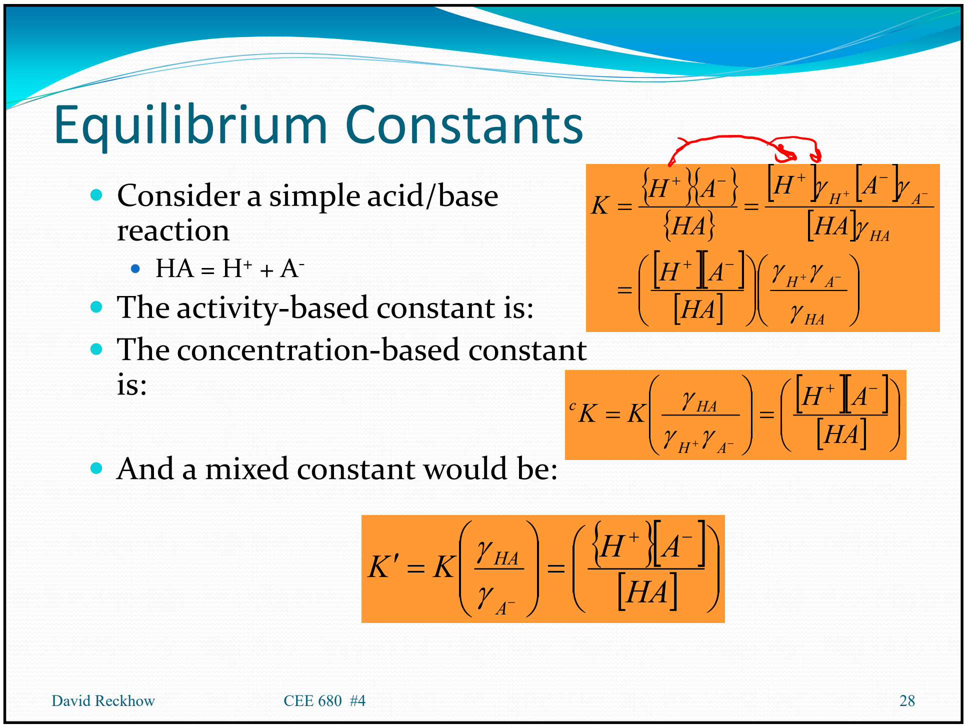
$$I = \tfrac{1}{2}\sum m_i z_i^2$$



Correlations for ionic strength

I

- μ vs. specific conductance: Russell Approximation
  - $\mu = 1.6 \times 10^{-5} \times K$ (in μmho/cm)
- μ vs. TDS: Langlier approximation
  - $\mu \sim 2.5 \times 10^{-5} \times TDS$ (in mg/L)



Equilibrium Constants

- Consider a simple acid/base reaction
  - $HA = H^+ + A^-$
- The activity-based constant is:

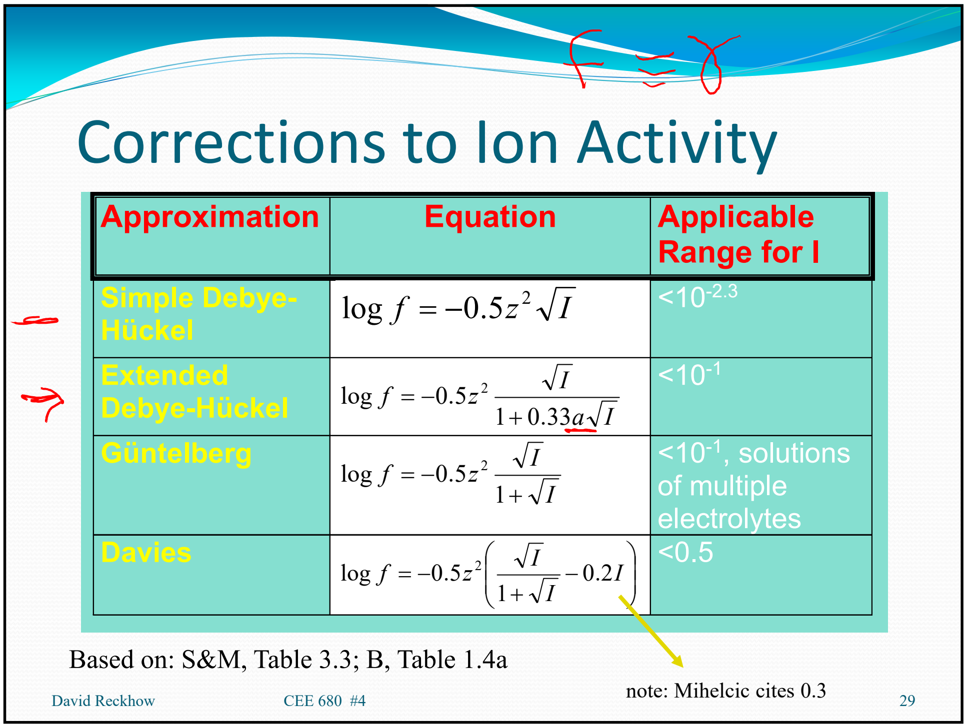
$$K = \frac{\{H^+\}\{A^-\}}{\{HA\}} = \frac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}} = \left(\frac{[H^+][A^-]}{[HA]}\right)\left(\frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}\right)$$

- The concentration-based constant is:

$$^cK = K\left(\frac{\gamma_{HA}}{\gamma_{H^+}\gamma_{A^-}}\right) = \left(\frac{[H^+][A^-]}{[HA]}\right)$$

- And a mixed constant would be:

$$K' = K\left(\frac{\gamma_{HA}}{\gamma_{A^-}}\right) = \left(\frac{\{H^+\}[A^-]}{[HA]}\right)$$



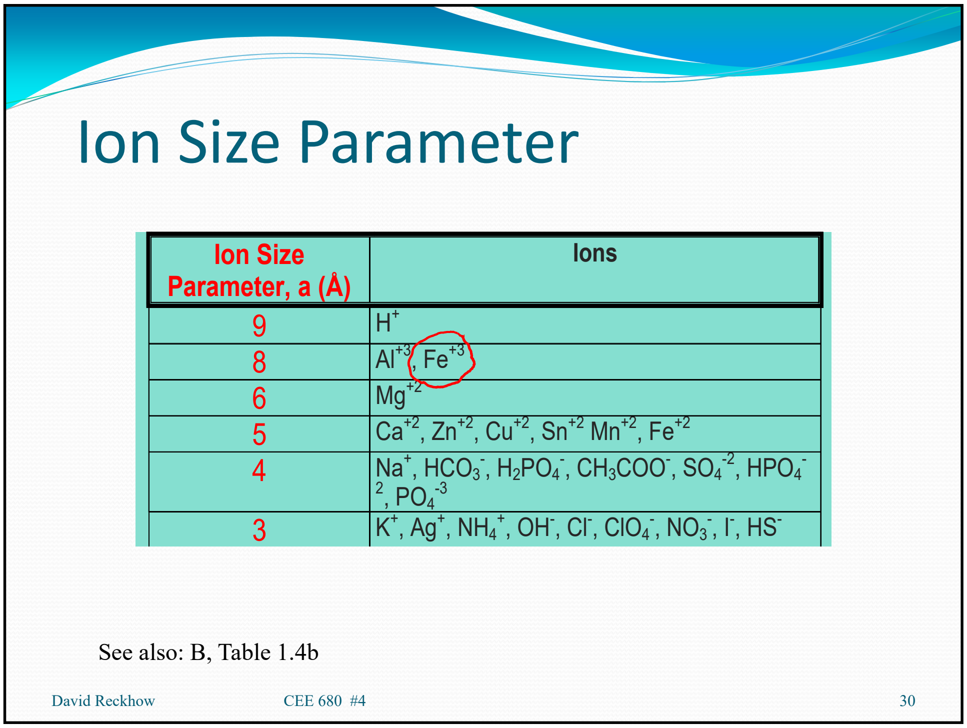
$f = \gamma$

Corrections to Ion Activity

Approximation	Equation	Applicable Range for I
Simple Debye-Hückel	$\log f = -0.5z^2\sqrt{I}$	$<10^{-2.3}$
Extended Debye-Hückel	$\log f = -0.5z^2 \dfrac{\sqrt{I}}{1+0.33a\sqrt{I}}$	$<10^{-1}$
Güntelberg	$\log f = -0.5z^2 \dfrac{\sqrt{I}}{1+\sqrt{I}}$	$<10^{-1}$, solutions of multiple electrolytes
Davies	$\log f = -0.5z^2 \left(\dfrac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$	<0.5

Based on: S&M, Table 3.3; B, Table 1.4a

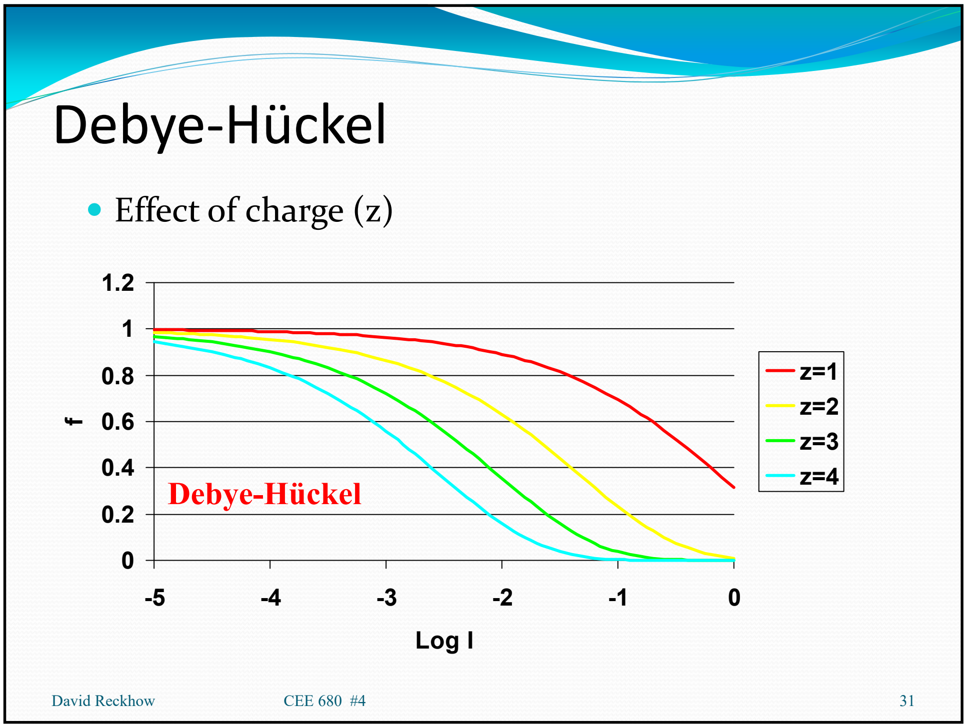
note: Mihelcic cites 0.3



Ion Size Parameter

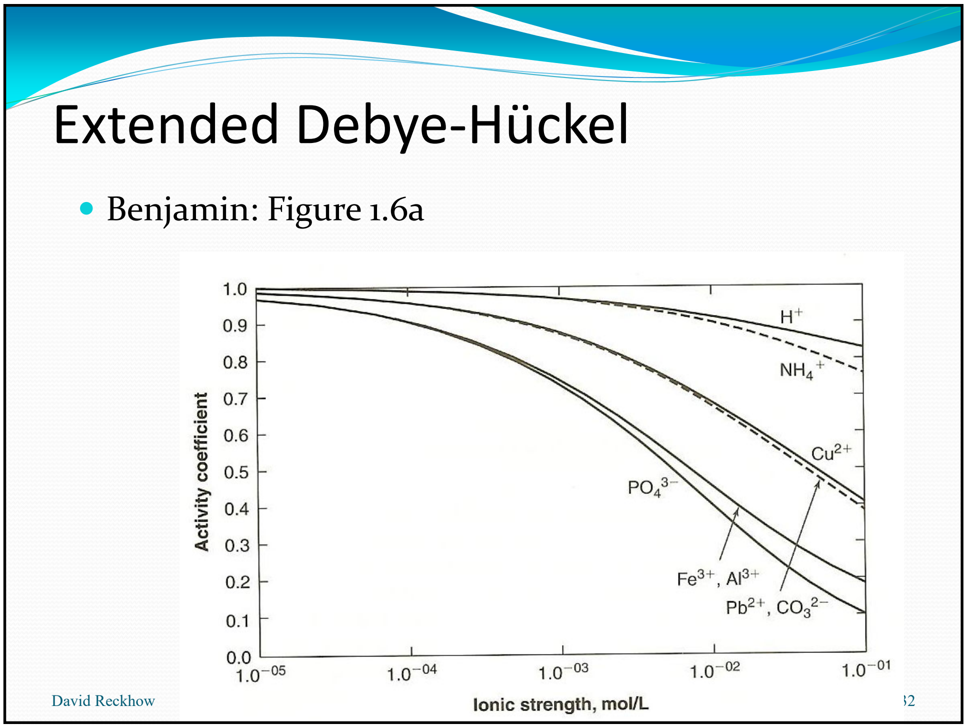
Ion Size Parameter, a (Å)	Ions
9	H^+
8	Al^{+3}, Fe^{+3}
6	Mg^{+2}
5	Ca^{+2}, Zn^{+2}, Cu^{+2}, Sn^{+2} Mn^{+2}, Fe^{+2}
4	Na^+, HCO_3^-, $H_2PO_4^-$, CH_3COO^-, SO_4^{-2}, HPO_4^{-2}, PO_4^{-3}
3	K^+, Ag^+, NH_4^+, OH^-, Cl^-, ClO_4^-, NO_3^-, I^-, HS^-

See also: B, Table 1.4b



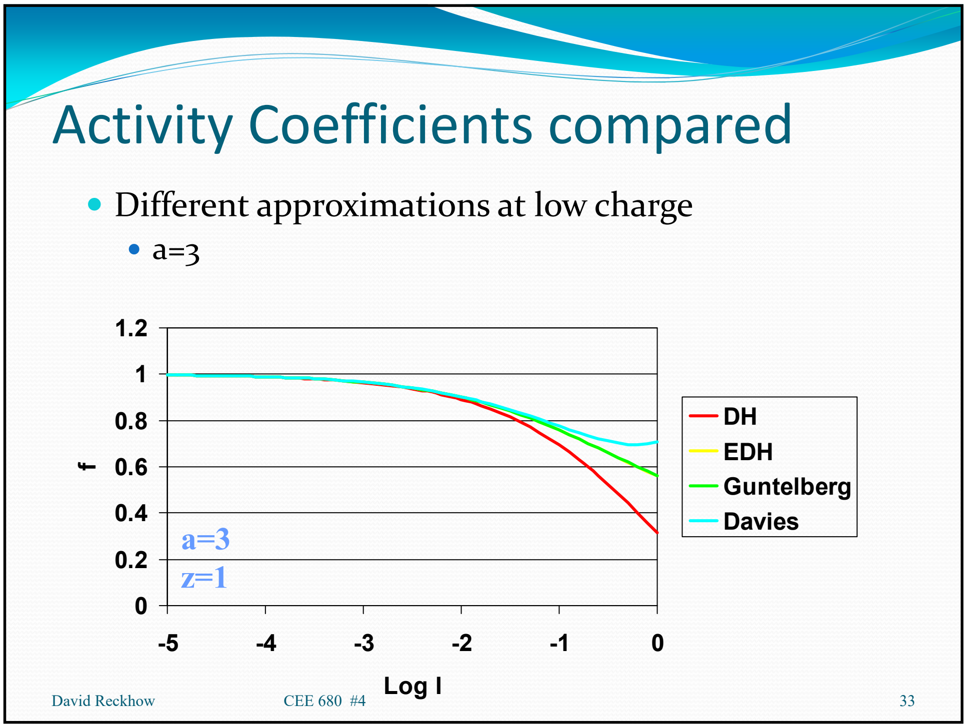
Debye-Hückel

- Effect of charge (z)



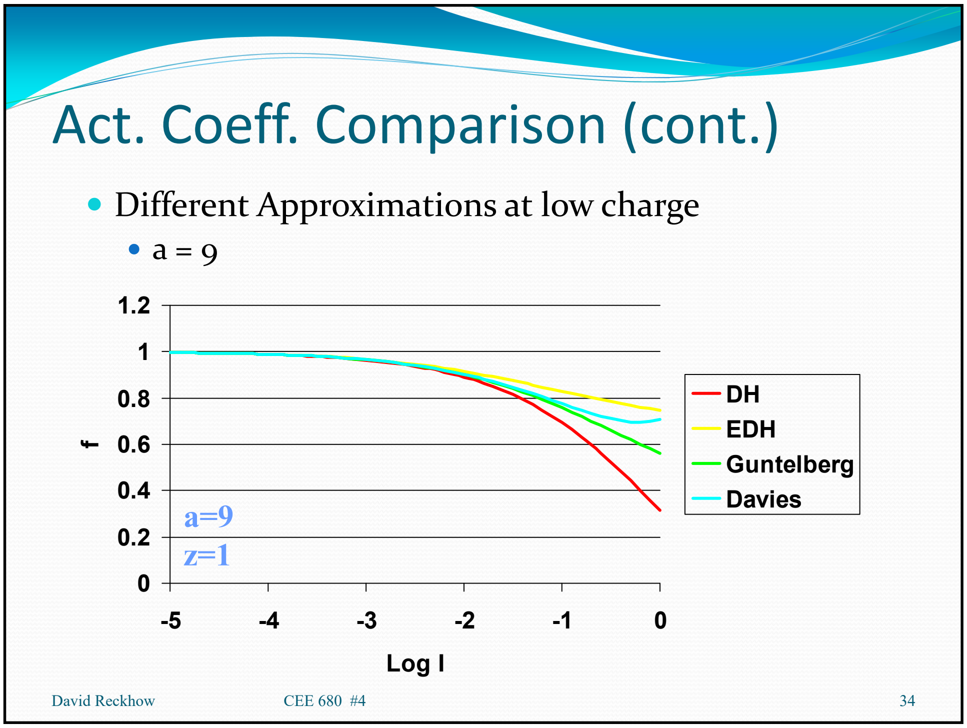
Extended Debye-Hückel

- Benjamin: Figure 1.6a



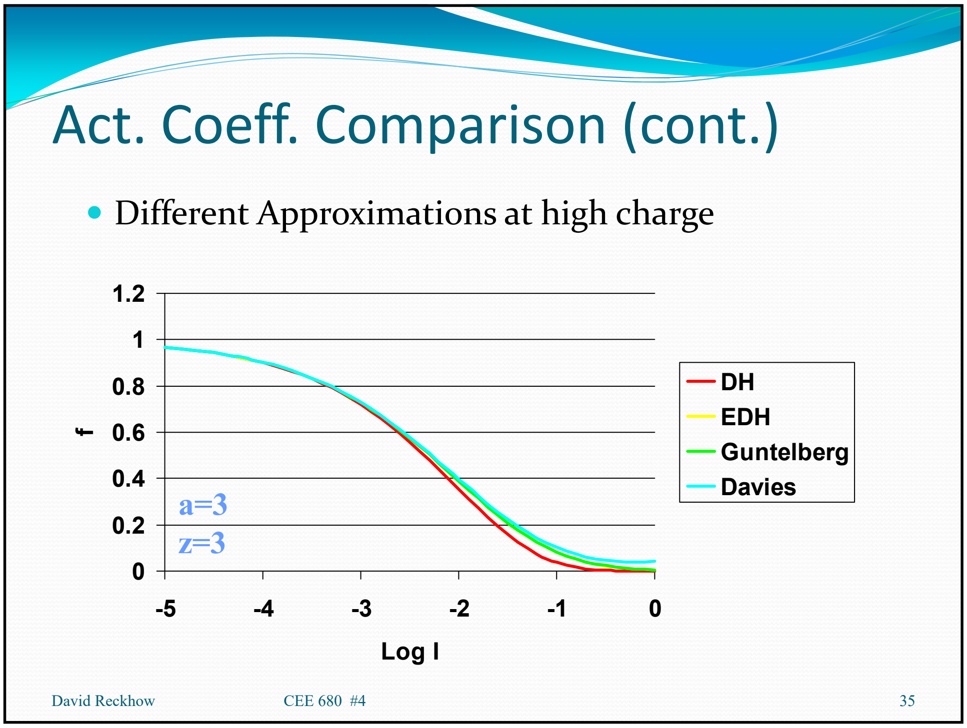
Activity Coefficients compared

- Different approximations at low charge
  - a=3



Act. Coeff. Comparison (cont.)

- Different Approximations at low charge
  - a = 9



Act. Coeff. Comparison (cont.)

- Different Approximations at high charge

Calcluation

- What is the activity coefficient for ferric iron in a solution of 0.1 M NaCl?
  - Solution
    - Use Extended Debye-Huckel

$$\log f = -0.5z^2 \frac{\sqrt{I}}{1 + 0.33a\sqrt{I}}$$

    - Determine value of "a" and "I"

$a = 8$

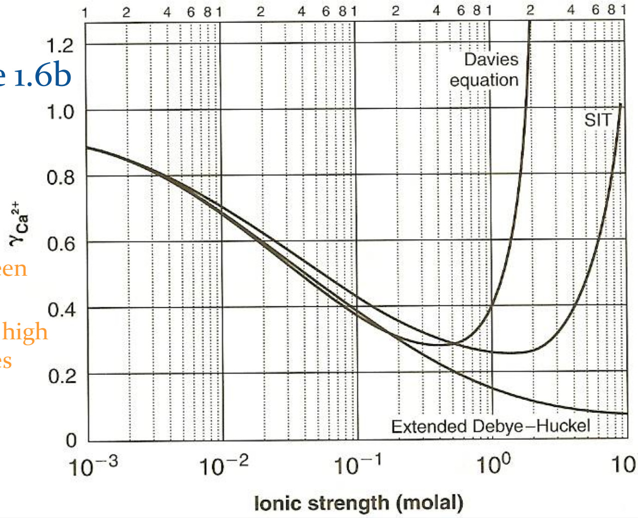
$I = 0.1$

$\log f = 0.776$

$f = 0.168$

Comparison: $CaCl_2$ dissolution

- Benjamin, Figure 1.6b
  - SIT is the specific interaction model
    - Incorporates interactions between specific ions
    - Quite accurate for high brines, but requires more coefficients



Activity Coefficients (cont.)

- For neutral species:
  - logγ = kI
    - k is a function of species, T and P
      - k=0.13 for O_2 in NaCl
        - in fresh water, I=0.002, γ_{O_2} = 1.0006
- Molar vs. Molal
    - in principle, activity predictions are based on molal concentrations (mole/kg solvent), but since we are often most concerned with dilute solutions, we frequently use molar concentrations

Salting out Coefficients

Compound	*k_s (L/mole)*	*Reference*
Tetrachloroethene	0.213	Gossett, 1987
Trichloroethene	0.186	Gossett, 1987
1,1,1-Trichloroethane	0.193	Gossett, 1987
1,1-Dichloroethane	0.145	Gossett, 1987
Chloroform	0.140	Gossett, 1987
Dichloromethane	0.107	Gossett, 1987
Benzene	0.195	Schwarzenbach et al., 1993
Toluene	0.208	Schwarzenbach et al., 1993
Naphthalene	0.220	Schwarzenbach et al., 1993
Oxygen	0.132	Snoeyink & Jenkins, 1980

Activity for isotopes

- Most subtle of the effects
- For saline waters (chloride is counterion)
  - Deuterium

$$ln\frac{\gamma({}^{2}H\,{}^{1}H^{16}O)}{\gamma({}^{1}H\,{}^{1}H^{16}O)} = 0.0022(Na^{+}) + 0.0025(K^{+})$$

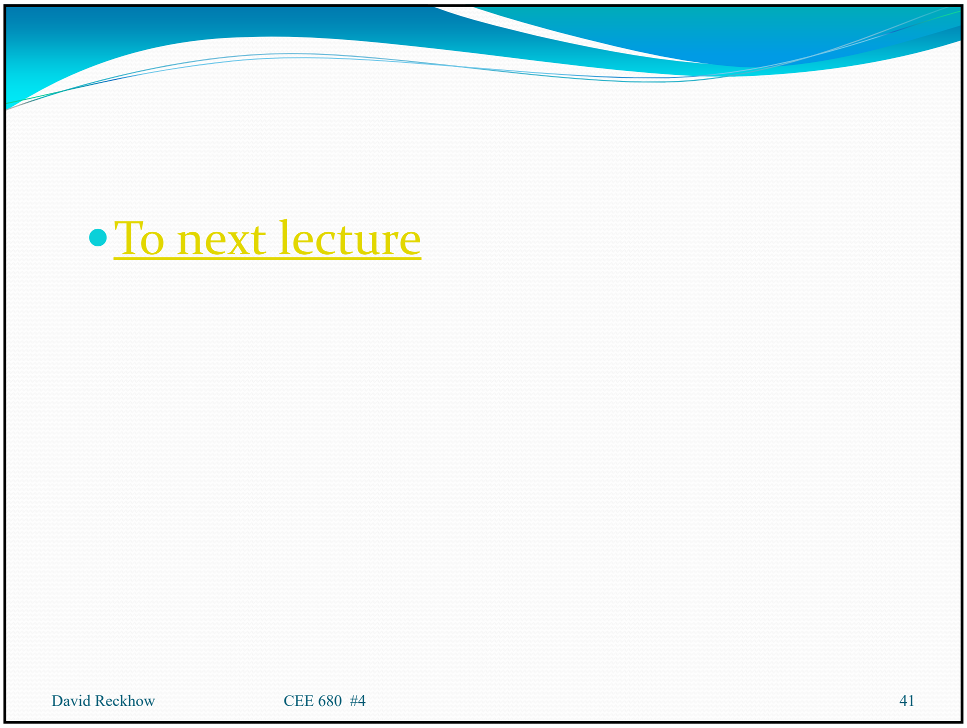
$$+0.0051(Mg^{+2}) + 0.0061(Ca^{+2})$$

  - Oxygen-18

$$ln\frac{\gamma({}^{1}H\,{}^{1}H^{18}O)}{\gamma({}^{1}H\,{}^{1}H^{16}O)} = 0.0016(K^{+}) - 0.0111(Mg^{+2})$$

$$-0.0047(Ca^{+2})$$

  - Where () represents the molal concentration (moles/Kg-water)



- To next lecture