# Introduction

Course guide

- Instructor: 최용주, 35-307, ychoi81@snu.ac.kr

- TA: 박서연, 35-517, sy1216@snu.ac.kr

- Course material
  – Lecture notes: uploaded on eTL prior to the class (go paper-less!)
  – Textbook: Principles of Environmental Engineering and Science, 4th ed.

Textbook

[ENG]

Mackenzie L. Davis and Susan J. Masten, Principles of Environmental Engineering and Science, 4th ed., McGraw-Hill, 2019
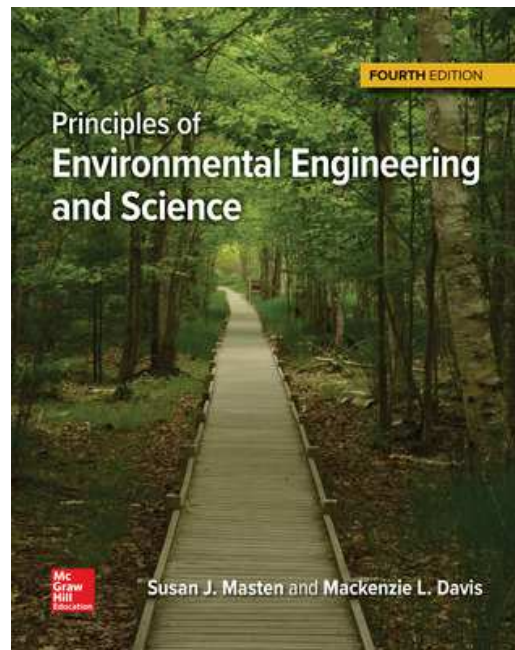
[KOR]

박제량, 최용주 등(역), 환경공학 및 과학 4판, 교문사, 2022

Office hour

- 5:00-5:30 pm Mon & 9:00-9:30 am Fri

- Via Zoom

- With the instructor
  - Announcement will be made for cancellation; use emails for Q&A when office hour is cancelled

Zoom link:

https://snu-ac-kr.zoom.us/j/8675573197

(Meeting ID 867 557 3197)

Evaluation

- Midterm [30%] / Final [30%]

- Homework assignments [15%]

- Team project [15%]

- Attendance [10%]
  - Not showing up for >1/3 of class dates → F
  - Not showing up for >5 class dates → B0 or lower
  - 3 lates = 1 absence

- Plagiarism & cheating: no credit

Team project overview

- Solution design for current environmental problems

- Can be either institutional or engineering solution (or both)

- Team of 4-5 students

- Select a **specific** topic

- Begin on Week 13, includes in-class "advised" discussion

- Presentation on Week 15

In this course...

We will focus on principles of environmental chemistry and biology and their engineering applications that help improving human health and environmental soundness

But.. then..

why Department of **Civil** and **Environmental** Engineering?

Environmental engineering

- It stems from civil engineering!

- Mid-1800s to mid-1900s: sanitary engineering (focused on providing safe drinking water and drainage of wastewater)

Roman waterway system

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Environmental engineering

Application of engineering principles to improve and maintain the environment for the protection of human health and at-risk ecosystems

- Then, what is the engineering principle?
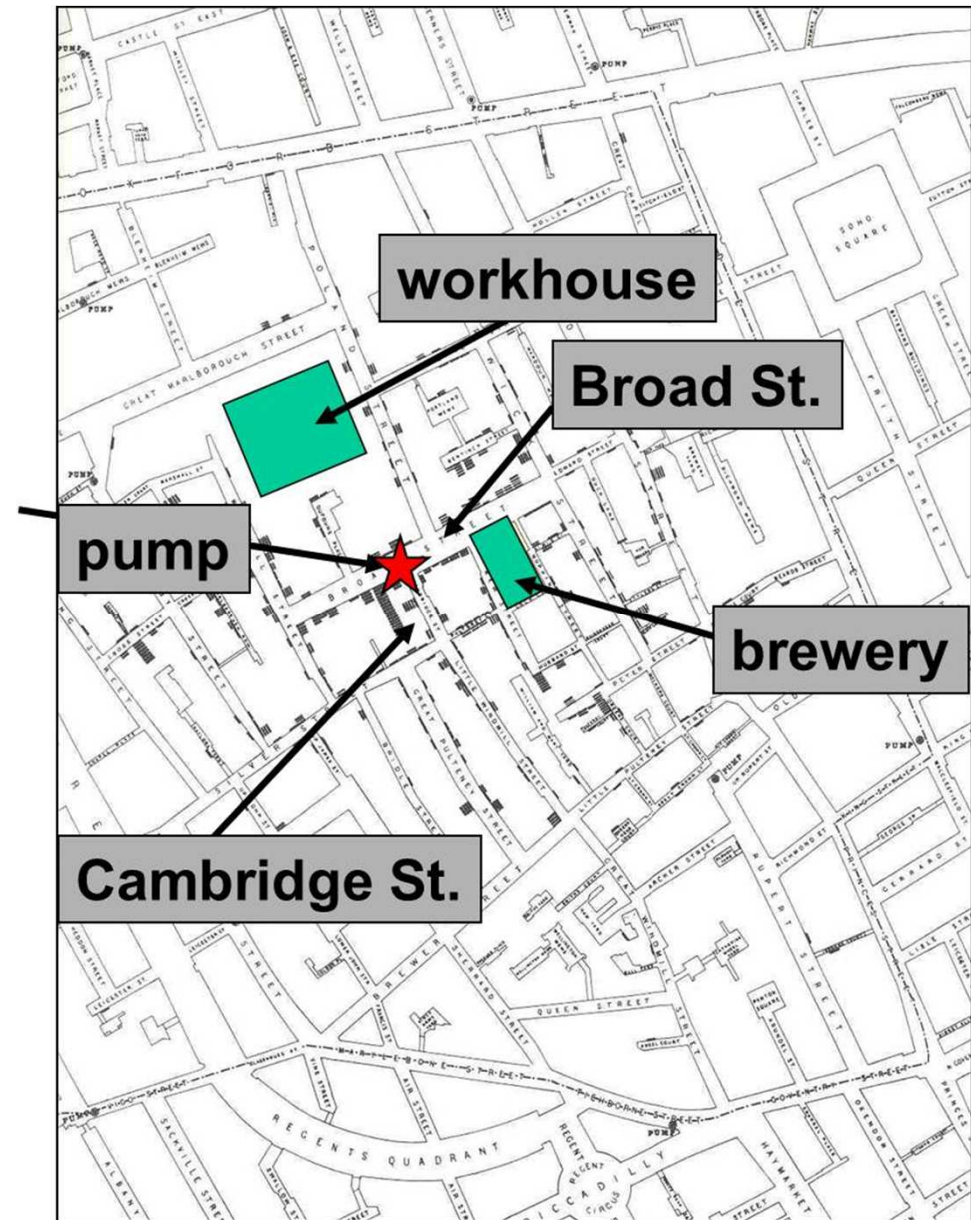
Course objectives

- General background on environmental science and engineering

- Understand principles of environmental science

- Understand causes, effects, and engineering solutions for environmental problems

- Local to global scale
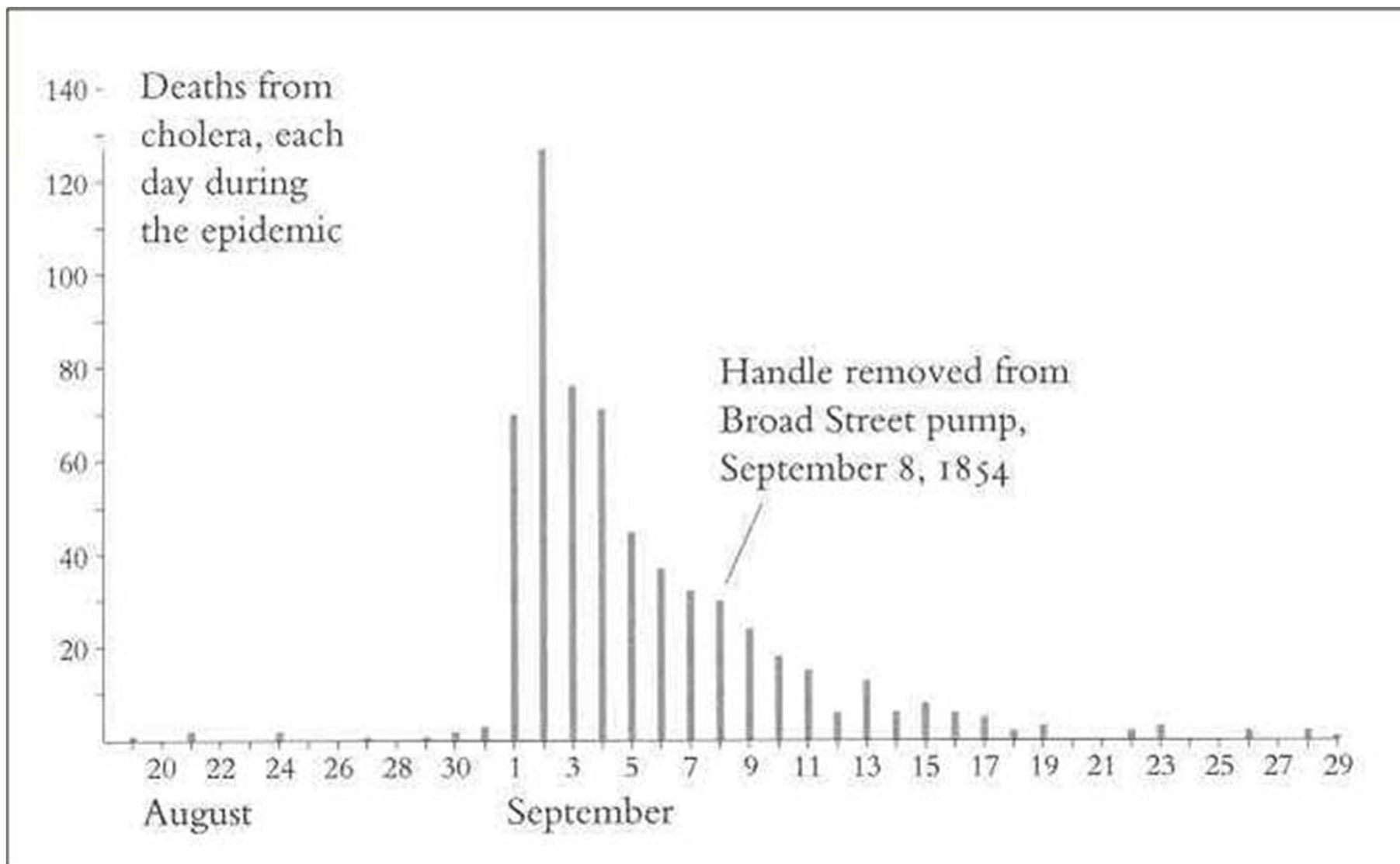
- Water, air, soil, waste, noise, …

Pioneers of environmental sci. & eng.

- Dr. John Snow
  - Frequent cholera outbreaks in Europe on 19th century: foul air was commonly believed as a reason
  - Studied Cholera outbreak in London (1853)
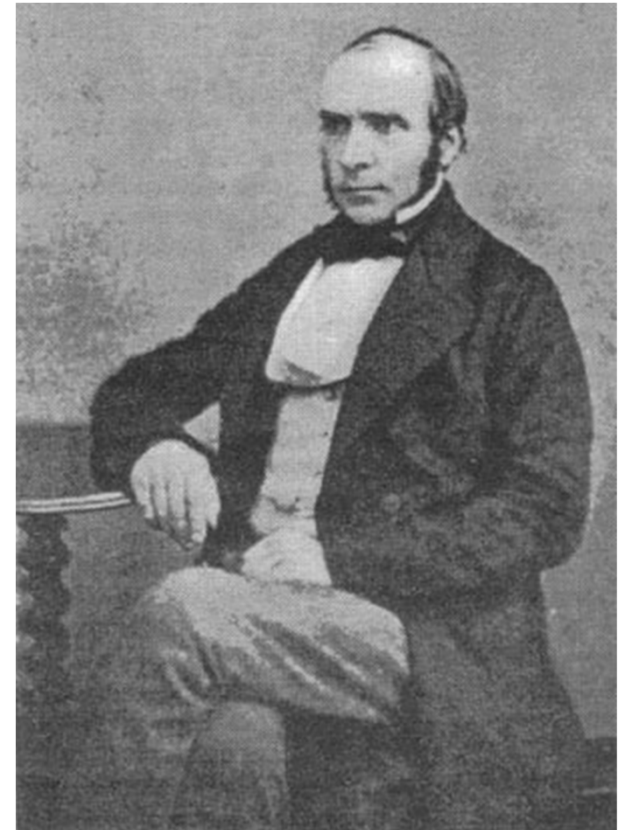
- Tracked 83 victims: most of them obtained water from a hand pump located on Broad St.
- Low incidence at a workhouse and the Lion Brewery: own water supply

140 — Deaths from
cholera, each
120 — day during
the epidemic

Handle removed from
Broad Street pump,
September 8, 1854

20   22   24   26   28   30   1   3   5   7   9   11   13   15   17   19   21   23   25   27   29

August   September

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Great medical advances in modern age

1. Sanitation (clean water and sewage disposal) – 15.8%

2. Antibiotics – 15%

3. Anaesthesia – 14%

4. Introduction to vaccines – 12%

5. Discovery of the structure of DNA – 9%

(British Medical Journal, 2007)

Environ. Eng. history in Korea

- Rapid economic growth since 1960

- Before 1980: most sewage and wastewater ran directly to rivers

Nakdong-river phenol outbreak

1차 페놀오염은 1991년 3월 16일 경상북도 구미시 구포동에 있는 두산전자의 페놀원액 저장탱크에서 페놀수지 생산 공장으로 페놀원액을 공급하는 과정에서 평소 사용하던 지상 파이프가 고장나, 예비용 지하파이프를 사용 하던 중 연결부에서 파이프가 파열되어 30톤이 유출되었다. 페놀원액이 대구 상수원인 다사취수장으로 흘러듦으로써 수돗물을 오염시켰다. 수돗물에서 악취가 난다는 신고를 받은 취수장측은 원인 규명도 하지 않고 염소를 다량 투입하였다.

페놀은 염료나 수지를 만들 때 쓰이는 특유의 냄새를 지닌 유기물질이다. 페놀이 정수장에서 염소와 화학반응을 일으켜 만들어지는 클로로페놀은 페놀보다 악취가 훨씬 심하고, 농도 1ppm을 넘으면 암, 중추신경장애 등을 일으키는 물질이다. 오염된 정수장 물이 대구시 거의 모든 지역에 식수로 공급되어, 일부 주민들은 두통과 구토 증세를 보이기도 하였다. 2차 페놀오염은 두산전자가 다시 조업을 시작한지 5일 만인 4월 22일 발생하였다. 부실 보수공사로 인해 페놀탱크 이음새 부분이 파열되어 페놀원액이 다시 낙동강으로 유입되면서 대구지역에 식수공급이 중단되었다.

이 사고로 많은 피해보상과 자연유산, 임신중절 등을 하기도 하였으며, 두산그룹 회장이 물러나고, 환경처 장차관이 인책, 경질되었다. 취수장을 오염시킨 페놀은 낙동강을 타고 흘러 밀양, 함안, 부산, 마산을 포함한 영남 전 지역이 페놀 파동에 휩쓸리게 되었다.

이 사건을 계기로 음용수 검사항목의 문제가 본격적으로 제기 되었을 뿐 아니라「환경범죄의 처벌에 관한 특별조치법」이 제정되었으며, 환경문제의 심각성에 대한 국민들의 경각심이 고조되었다.

(국가기록원, 2007)

Hebei Spirit oil spill

2007년 12월7일 오전 충청남도 태안군 만리포 북서방 8km 해상에서 삼성 T-5호 및 삼호 T-3호 등 예인선 2척이 해상 크레인 부선 삼성 1호를 병렬로 연결하여 항해하던 중, 좌측에 있던 삼성 T-5호와의 예인줄이 절단되는 사고가 발생하였다. 이로 인해 예인 중이던 부선 크레인이 통제력을 상실하면서 대산항 입항을 위해 정박 중이던 홍콩선적 유조선 허베이 스피리트(Hebei Sprit)호와 충돌하였으며, 유조선에 선적되어 있던 약 12,547kℓ의 원유가 해상으로 유출되는 국내 최대 해양오염사고가 발생하였다.

이전에는 1995년 여수에서 발생한 씨프린스호 사고로 5,053톤의 유류가 유출된 것이 국내 최대의 기록이었는데, 본 사고는 씨프린스호 사고의 2배가 넘는 유류오염사고로서 유출된 원유가 국내 유일의 해안국립공원지역인 청정지역에서 발생했다는 점에서 그 심각성이 매우 큰 사건이었다.

원유유출 사고 후 2007년 12월 11일 충남 태안, 서산, 보령, 서천, 홍성, 당진 등 6개 지역이 특별재난지역으로 선포되었고, 재해대책 예비비 및 주민 방제인건비 등을 지급하며 정부 차원의 방제대책이 마련되었다. 이밖에도 100만 명 이상의 자원봉사자들이 태안반도의 방제 및 복구 작업에 힘을 모았다.

2009년 4월 대법원은 삼성1호가 크레인 절단을 초래한 것이 선박충돌의 주된 원인이지만, 허베이 스피릿호의 소극적인 피항 태도 및 기름오염에 대한 대응조치가 미흡했다는 점에도 책임을 물어 쌍방과실이 성립한다고 보고, 「해양오염방지법」위반 등으로 양측 모두 유죄를 선고하였고, 해양오염방지법 위반에 따른 3,000만원의 벌금을 부과하였다. 또한 서울중앙지법은 삼성중공업의 태안 사고에 대한 배상책임을 제한해달라고 낸 선박책임제한절차(해상 선박사고의 피해보상책임을 일정수준으로 제한하는 상법상의 절차로 최고배상제한액은 50억원) 신청을 받아들여, 삼성중공업 측의 법적 배상책임금액을 56억 원(배상제한액 50억 원에 법정이자를 포함된 금액)으로 결정하였다.

Environ. Eng. history in Korea
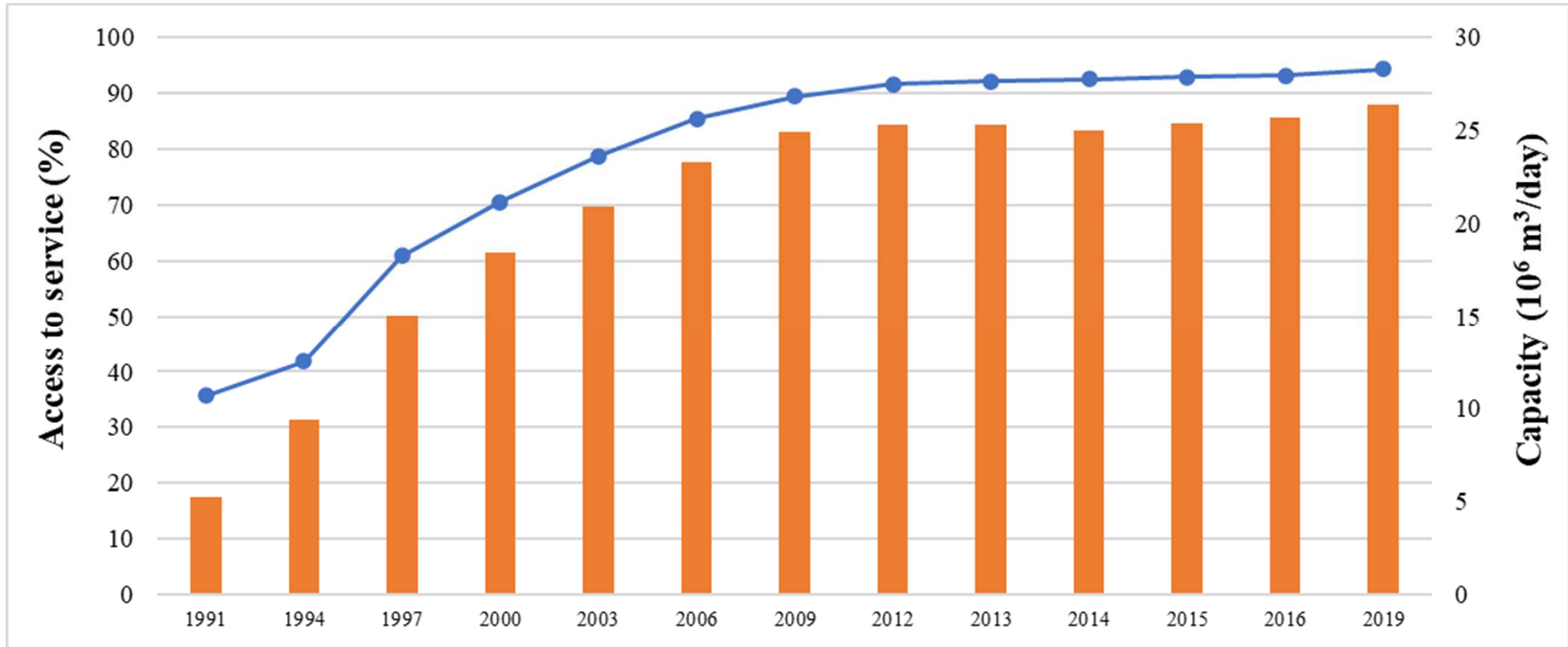
e-나라지표, www.index.go.kr

● —— Access to sewer service

■ Sewage treatment capacity

Almost nothing in 1970s (& no stat.)

→ 35.7% in service in 1991

→ 94.3% in service in 2019

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Is it enough?

Suggested readings

[ENG] pp. 3 – 13

[KOR] pp. 3 – 13

Next class

Basic chemistry concepts I

- Chemistry – basics of basics
- Chemical reactions
- Equilibrium chemistry

Basic Chemistry Concepts I

Basic chemistry concepts

- Chemistry – basics of the basics
- Chemical reactions
- Equilibrium chemistry

Mole & molarity

- Mole = Avogadro's number (6.02×10^{23}) of molecules
- Molarity (M) = number of moles per <u>liter</u> of <u>solution</u> (mole/L)

  cf) molality (m) = number of moles per <u>kg</u> of <u>solvent</u>

Other concentration units for water

- Weight percent, *P*

$$P = \frac{W}{W + W_0} \times 100\%$$

W = mass of substance (g)
W$_0$ = mass of solute (g)

- Mass concentration: g/m^3, mg/L, µg/L, ng/L, …

- ppm, ppb, ppt

- Normality, *N* (acid-base reaction)

$$N = nM$$

n = no. of protons transferred

Activity

- Determines the tendency for a reaction to occur
- Represented by { } (cf. molarity by [ ])
- In dilute aqueous solutions, the ions do not significantly interact with one another:

  $\{i\} \approx [i]$

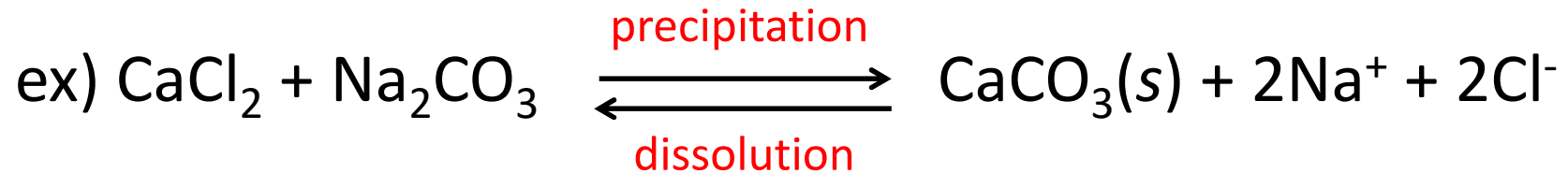- As concentration increases, the ion-ion interaction becomes more significant:

  $\{i\} = \gamma_i \cdot [i]$ where γ_i = activity coefficient

Balancing chemical reactions

$Ca(HCO_3)_2 + NaOH = Ca(OH)_2 + NaHCO_3$
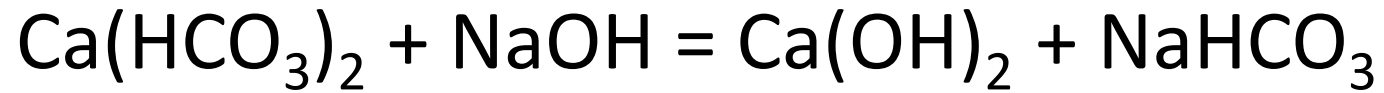
Types of chemical reactions

- Precipitation-dissolution reactions

ex) $CaCl_2 + Na_2CO_3$ $\underset{\text{dissolution}}{\overset{\text{precipitation}}{\rightleftharpoons}}$ $CaCO_3(s) + 2Na^+ + 2Cl^-$
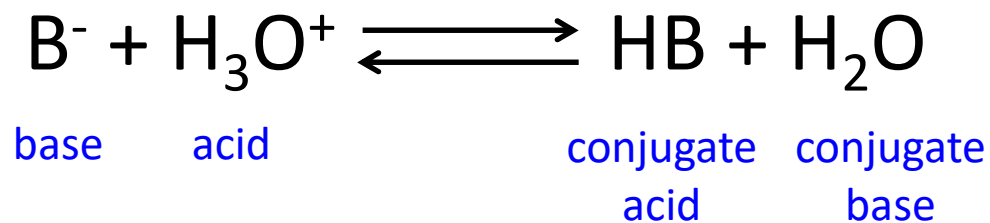
Usage: softening, phosphorous removal, heavy metal removal, …

Acid-base reactions

- Brønsted-Lowry acid: any substance that can donate a proton (i.e., proton donor)

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

   acid   base   conjugate   conjugate
                                  base   acid
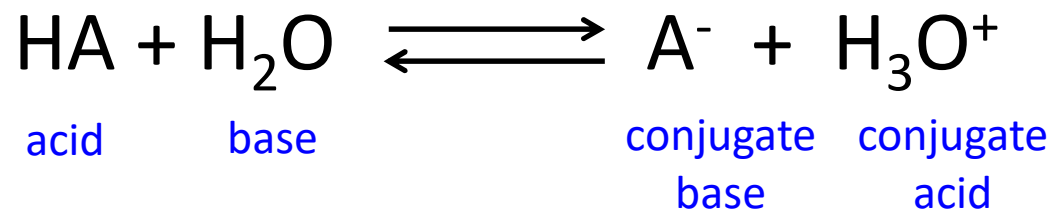
- Brønsted-Lowry base: any substance that can accept a proton (i.e., proton acceptor)

$$B^- + H_3O^+ \rightleftharpoons HB + H_2O$$

 base   acid   conjugate conjugate
   acid   base

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cf) other definitions of acid & base

- Arrhenius definition
  - Arrhenius acid: a substance that dissociates in water to release protons (H^+)
  - Arrhenius base: a substance that dissociates in water to release hydroxide ions (OH^-)

- Lewis definition
  - Lewis acid: electron pair acceptor
  - Lewis base: electron pair donor
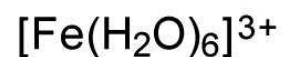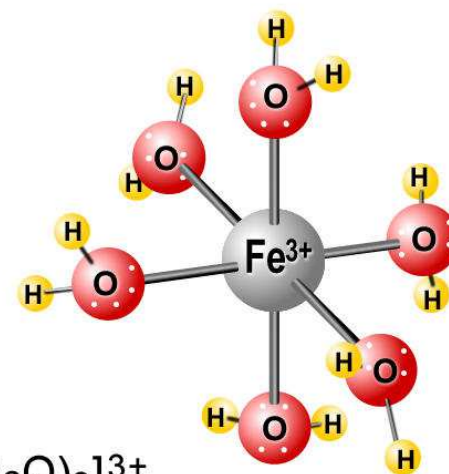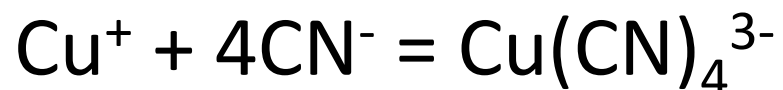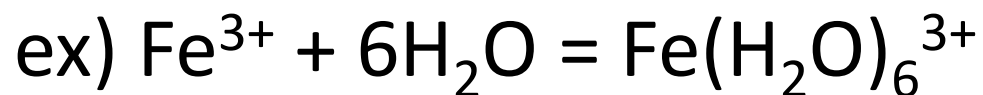
Water as both acid & base

- Water is amphoteric – can be either an acid or a base

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

acid   base   conjugate conjugate
base   acid
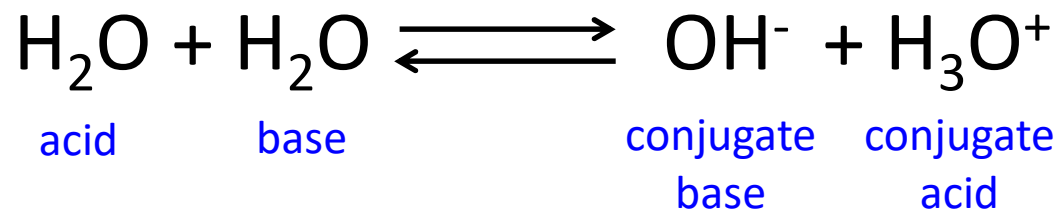
- pH ≡ -log{H$^+$}   ("p" denotes "-log")

Complexation reactions

- Coordination of two or more atoms, molecules, or ions resulting in the formation of a more stable product

ex) $Fe^{3+} + 6H_2O = Fe(H_2O)_6^{3+}$

$Cu^+ + 4CN^- = Cu(CN)_4^{3-}$

$[Fe(H_2O)_6]^{3+}$
Octahedral

©NCSSM 2003

- Complex ion = a metal ion (Lewis acid) coordinated with ligands (Lewis bases)

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Complexation reactions - implications

- Many metal ions exist as complex ions in water (metal aquo complex)

  ex) $[Cr(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Co(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$

- Environmental significance: complexation of metals affects the uptake, biodegradability, toxicity, and mobility of the metal
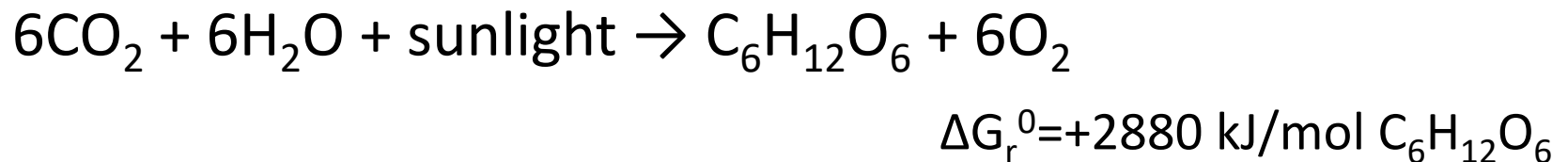
Oxidation-reduction (redox) reactions

- Involves changes in the oxidation state
- Essential for life: photosynthesis and respiration are redox reactions!

respiration using glucose:

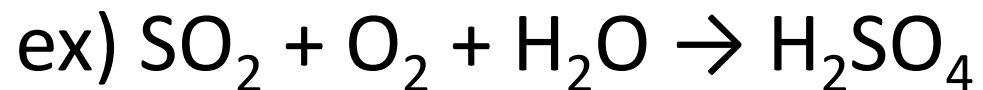$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \Delta G_r^0 = -2880 \text{ kJ/mol } C_6H_{12}O_6$$

photosynthesis of glucose:

$$6CO_2 + 6H_2O + sunlight \rightarrow C_6H_{12}O_6 + 6O_2$$

$$\Delta G_r^0 = +2880 \text{ kJ/mol } C_6H_{12}O_6$$

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Balancing redox reactions

- Have to consider <u>electron balance</u> in addition to atom balance!

ex) $SO_2 + O_2 + H_2O \rightarrow H_2SO_4$

Chemical equilibrium

- For a reversible reaction

  aA + bB $\rightleftharpoons$ cC + dD
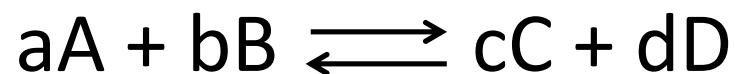
  at chemical equilibrium,

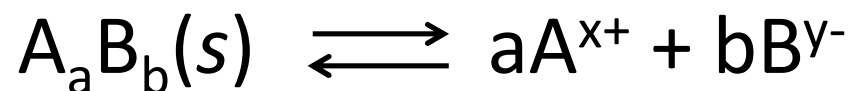 rate(forward reaction) = rate(reverse reaction)

- Equilibrium constant, K

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

For pure solid, activity = 1
For gases, activity = partial pressure

Chemical equilibrium: solubility

- For a precipitation-dissolution reaction

$A_aB_b(s) \rightleftharpoons aA^{x+} + bB^{y-}$

$$K = \frac{\{A^{x+}\}^a\{B^{y-}\}^b}{\{A_aB_b\}}$$

note $\{A_aB_b\} = 1$ (pure solid)

- Solubility product, $K_s = \{A^{x+}\}^a\{B^{y-}\}^b$

Ionic strength

- We can measure [ ], not { }. How to correlate { } with [ ]?
- Recall {i} = γ_i[i]:

$$K_s = \{A^{x+}\}^a \{B^{y-}\}^b = (\gamma_A [A^{x+}])^a \cdot (\gamma_B [B^{y-}])^b$$

- γ_i significantly smaller than 1 in highly concentrated solutions because of ion-ion interactions

- Ionic strength, I : measure of interaction among ions in a solution

$$I = \frac{1}{2} \sum_i C_i z_i^{\,2}$$

C_i = molarity of the ith ion

z_i = charge of the ith ion

Calculating activity coefficients

- Davies equation (for *I* < 0.5):

$$log\gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

$A \approx 0.5$ for water at 25°C

z_i = charge of the ion

There are many approximations available, verified at different ranges of ionic strength. Let's use Davies equation for this class.

Ionic strength & activity coefficient

Q: For the following solutions, calculate i) the ionic strength of the solution and ii) activity of each ion using the Davies equation (A=0.5).

  a) 1 mM NaCl

  b) 1 mM $CaCl_2$

Selected solubility products (@ 25ºC)

Substance	Equilibrium Reaction	pK_s	Application
Aluminum hydroxide	$Al(OH)_3 (s) \rightleftharpoons Al^{3+} + 3OH^-$	32.9	Coagulation
Aluminum phosphate	$AlPO_4 (s) \rightleftharpoons Al^{3+} + PO_4^{3-}$	22.0	Phosphate removal
Calcium carbonate (aragonite)	$CaCO_3 (s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	8.34	Softening, corrosion control
Ferric hydroxide	$Fe(OH)_3 (s) \rightleftharpoons Fe^{3+} + 3OH^-$	38.57	Coagulation, iron removal
Ferric phosphate	$FePO_4 (s) \rightleftharpoons Fe^{3+} + PO_4^{3-}$	21.9	Phosphate removal
Magnesium hydroxide	$Mg(OH)_2 (s) \rightleftharpoons Mg^{2+} + 2OH^-$	11.25	Removal of calcium and magnesium
Dolomite $(CaMg(CO_3)_2)$ (ordered)	$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	17.09	Weathering of dolomitic minerals
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ \rightleftharpoons 2Al^{3+} + 2Si(OH)_4 + H_2O$	7.44	Weathering of kaolinite clays
Gypsum	$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$	4.58	Weathering of gypsum minerals

Chemical equilibrium: solubility

Q: You added 30 g of $CaCO_3$ in water of make 1.00 L solution containing 0.01 M NaCl. Assuming Ca^{2+} in solution is at equilibrium with $CaCO_3(s)$, what would be the Ca^{2+} concentration?

(T =25°C, pK_s for $CaCO_3$ = 8.48)

Suggested readings

[ENG] pp. 41 – 54, 71 – 74

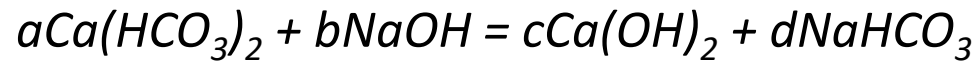[KOR] pp. 35 – 49, 68 – 71

Next class

Basic chemistry concepts II

- Equilibrium chemistry – acid-base reaction, Henry's law
- Reaction kinetics
- Carbonate system and alkalinity

Slide#5 solution

Basic rule: conservation of matter (atoms)

$aCa(HCO_3)_2 + bNaOH = cCa(OH)_2 + dNaHCO_3$

Ca: a = c	*(1)*
Na: b = d	*(2)*
H: 2a + b = 2c + d	*(3)*
C: 2a = d	*(4)*
O: 6a + b = 2c + 3d	*(5)*

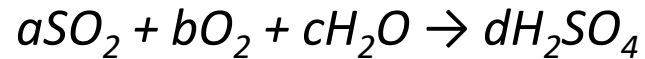*Four unknowns* → *three equations needed (obtain the ratio of each)*

e.g., use (1), (2) & (4): 2a = 2c = b = d (satisfies (3) & (5) as well)

→ $Ca(HCO_3)_2 + 2NaOH = Ca(OH)_2 + 2NaHCO_3$

Slide#13 solution

Basic rule: conservation of matter (atoms + electrons)

$aSO_2 + bO_2 + cH_2O \rightarrow dH_2SO_4$

    S: a = d   *(1)*

    O: 2a + 2b + c = 4d   *(2)*

    H: 2c = 2d   *(3)*

    e^-: (O_2 [0] + $4e^-$ $\rightarrow$ $2O^{2-}$) x b;   *(S^{4+} $\rightarrow$ S^{6+} + $2e^-$) x a*

      4b = 2a   *(4)*

e.g., use (1), (2) & (4): a = 2b = c = d (satisfies (2) as well)

$\rightarrow$ **$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$**
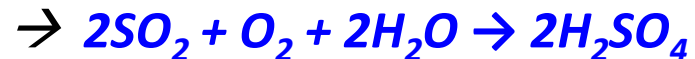
Slide#18 solution

a) 1 mM = 0.001 M NaCl

$$I = \frac{1}{2}[(C_{Na^+})(z_{Na^+})^2 + (C_{Cl^-})(z_{Cl^-})^2]$$

$$= \frac{1}{2}[(0.001\ M)\cdot(1^2) + (0.001\ M)\cdot(1^2)] = 0.001$$

$$\log \gamma_{Na^+} = -A z_{Na^+}^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$$

$$= -0.5 \cdot (1)^2 \left(\frac{\sqrt{0.001}}{1+\sqrt{0.001}} - 0.2 \cdot 0.001\right)$$

$$= 0.0152$$

$$\gamma_{Na^+} = 0.966$$

$$\{Na^+\} = \gamma_{Na^+}[Na^+] = 0.966 \cdot 0.001 = 9.66 \times 10^{-4}$$

Likewise, $\{Cl^-\} = 9.66 \times 10^{-4}$

b) 1 mM = 0.001 M $CaCl_2$

$$I = \frac{1}{2}[(C_{Ca^{2+}})(z_{Ca^{2+}})^2 + (C_{Cl^-})(z_{Cl^-})^2]$$

Because 0.001 M $CaCl_2$ dissolves in water to form 0.001 M Ca^{2+} & 0.002 M Cl^-

$$= \frac{1}{2}[(0.001\ M) \cdot (2^2) + (0.002\ M) \cdot (1^2)] = 0.003$$

$$\log \gamma_{Ca^{2+}} = -Az_{Ca^{2+}}^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$$

$$= -0.5 \cdot (2)^2 \left(\frac{\sqrt{0.003}}{1+\sqrt{0.003}} - 0.2 \cdot 0.003\right)$$

$$= 0.1027$$

$$\gamma_{Ca^{2+}} = 0.789, \quad \{Ca^{2+}\} = \gamma_{Ca^{2+}}[Ca^{2+}] = 7.89 \times 10^{-4}$$

$$\log \gamma_{Cl^-} = -0.5 \cdot (1)^2 \left(\frac{\sqrt{0.003}}{1+\sqrt{0.003}} - 0.2 \cdot 0.003\right) = -0.0257$$

$$\gamma_{Cl^-} = 0.943, \quad \{Cl^-\} = \gamma_{Cl^-}[Cl^-] = 1.89 \times 10^{-3}$$

Slide#20 solution

i) Assume ionic strength is negligible (activity = molarity)

$[Ca^{2+}] = [CO_3^{2-}]$

$K_s = 10^{-8.48} = [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}]^2$

[Ca²⁺] = 5.75 x 10⁻⁵ M

ii) Without the assumption

Let's assume NaCl is a sole contributor of ionic strength

$I = \frac{1}{2}[(0.01\ M) \cdot (1^2) + (0.01\ M) \cdot (1^2)] = 0.01$

$log\gamma_{Ca^{2+}} = log\gamma_{CO_3^{2-}} = -0.5 \cdot 2^2 \left(\frac{\sqrt{0.01}}{1+\sqrt{0.01}} - 0.2 \cdot 0.01\right) = -0.175$

$\gamma_{Ca^{2+}} = \gamma_{CO_3^{2-}} = 10^{-0.175} = 0.664$

$\{Ca^{2+}\} = \gamma_{Ca^{2+}}[Ca^{2+}] = 5.75 \times 10^{-5}$

[Ca²⁺] = 8.66 x 10⁻⁵ M

→ *the assumption for i) is not valid (34% underestimation)*

Now, let's check if the assumption that "NaCl is the sole contributor of ionic strength" is valid

Corrected ionic strength (include Na^+, Cl^-, Ca^{2+}, & CO_3^{2-}):

$I = \frac{1}{2}[(0.01\ M) \cdot (1^2) + (0.01\ M) \cdot (1^2) + (8.66 \times 10^{-5}\ M) \cdot (2^2) + (8.66 \times 10^{-5}\ M) \cdot (2^2)] = 0.01035$

$\log \gamma_{Ca^{2+}} = \log \gamma_{CO_3^{2-}} = -0.5 \cdot 2^2 \left(\frac{\sqrt{0.01035}}{1+\sqrt{0.01035}} - 0.2 \cdot 0.01035 \right) = -0.181$

$\gamma_{Ca^{2+}} = \gamma_{CO_3^{2-}} = 10^{-0.181} = 0.659$

$\gamma_{Ca^{2+}}[Ca^{2+}] = 5.75 \times 10^{-5}\ M$

[Ca²⁺] = 8.73 x 10⁻⁵ M (0.8% error – assumption is valid if we accept <5% error)

cf) accurate solution = 8.84 x 10⁻⁵ M. This solution can be obtained by iterative calculations (in other words, by repeating updating [Ca²⁺] and calculating new I, and then again updating [Ca²⁺] and calculating new I, and so on until the values converge).