

6_1 Chemistry of Geothermal Fluids

Recap:

1. Overall behavior of geothermal reservoirs - under production - Mechanisms of depletion
2. Lumped parameter models - pressure and heat recovery
3. Distributed parameter models - radial flow
4. Thermal breakthrough
5. Limits of heat rate recovery

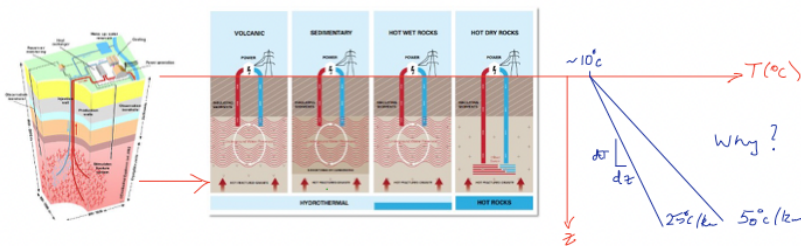
Movies:

??:

Resources: WG5

Motivation:

1. Motivation [10%] Provide context for the topic. *Use of relevant public domain videos* are a useful method for this. Why is this particular topic or sub-topic important in the broad view of geothermal energy engineering?



What chemical reactions and dissolution and precipitation impact:

1. Piping and wells
2. Surface facilities
3. Subsurface reservoirs - injection and recovery

Scientific Questions:

2. Scientific Questions to be Answered/Outline [10%] What questions arise from the motivation. What are the sub-topical areas that address these scientific questions.

Define rates of fluid flow and energy production with time - influenced by chemistry

1. Chemistry of geothermal fluids
2. Units of concentration
3. Chemical equilibrium and Law of Mass Action
 - A. Chemical activity
 - B. Affinity
4. Solubility
5. Kinetics and reaction rates
6. Reservoir/Plan response

1. Chemistry of geothermal fluids

TABLE 5.2

Chemical Composition of Waters from Diverse Geothermal Systems

Location	pH ^a	Na	K	Ca	Mg	Cl	B	SO ₄	HCO ₃	SiO ₂
Wairakei, New Zealand (W24)	8.3	1,250	210	12	0.04	2,210	28.8	28	23	670
Tauhara, New Zealand (TH1)	8.0	1,275	223	14	–	2,222	38	30	19	726
Broadlands, New Zealand (BR22)	8.4	1,035	224	1.43	0.1	1,705	51	2	233	848
Ngawha, New Zealand (N4)	7.6	1,025	90	2.9	0.11	1,475	1,080	27	298	464
Cerro Prieta, Mexico (CPM19A)	7.27	7,370	1,660	438	0.35	13,800	14.4	18	52	808
Mahia-Tongonan, Philippines (103)	6.97	7,155	2,184	255	0.41	13,550	260	32	24	1,010
Reykjanes, Iceland (8)	6.4	11,150	1,720	1,705	1.44	22,835	8.8	28	87	631
Salton Sea, California (IID1)	5.2	62,000	21,600	35,500	1,690	191,000	481.2	6	220	1,150
Paraso, Solomon Islands (A3)	2.9	136	27	51	11.1	295	5	300	–	81
Paraso, Solomon Islands (B4)	2.8	9	3	17	10	2	2	415	–	97

Sources: Henley, R.W. et al., *Fluid-Mineral Equilibria in Hydrothermal Systems*, vol. 1. Reviews in Economic Geology. Chelsea, MI: Society of Economic Geologists, 1984; Solomon Islands from Giggenschach, W.F., *Proceedings of the World Geothermal Congress*, Florence, Italy, 995–1000, 1995.

Note: All concentrations are in mg/kg. The paranthetical expressions are the identifiers for the wells from which the analyses were obtained.

^a This is the pH measured in the laboratory at 20°C and is not the pH of the fluid in the reservoir.

2. Units of concentration

By mass per liter of water: $\text{mg/L} \doteq 10^{-3} \text{g/L} \doteq \text{ppm}$
 $\mu\text{g/L} \doteq 10^{-6} \text{g/L} \doteq \text{ppb}$

Equivalent weight: $\frac{\text{Formula weight}}{\text{Electrical charge (of ions)}}$

Milliequivalents per liter: $\frac{\text{Concentration in mg/L}}{\text{Formula weight}}$

1-Molal: 1 mole solute in 1000 g (1 liter) of solvent

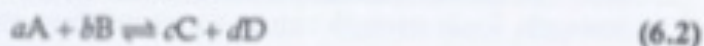
1-Molar: 1 mole solute in 1000 g () of solution

For dilute solution (less than seawater)

$$\text{Molality} = \frac{(\text{mg/L}) \times 1}{\text{Formula wt.}}$$

6.3 Chemical Equilibrium and the Law of Mass Action

The law of mass action states that the rate of a chemical reaction will be proportional to the active masses of the participating substances (Hem 1985). If there are two substances, A and B, reacting to form two other substances, C and D, and if the process is reversible, then the reaction can be written as



The rate of the forward reaction, R_1 , is

$$R_1 = k_1 [A]^a [B]^b \quad (6.3)$$

whereas the rate of the reverse reaction, R_2 , is

$$R_2 = k_2 [C]^c [D]^d \quad (6.4)$$

where:

[A] = active concentration of substance A

k_1 = proportionality constant for the forward reaction

k_2 = proportionality constant for the reverse

If the reaction progresses to a point where the forward reaction rate is equal to the reverse reaction rate, then

$$k_1 [A]^a [B]^b = k_2 [C]^c [D]^d \quad (6.5)$$

Equation 6.5 can be rearranged to yield the following expression:

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_1}{k_2} = K_{eq} \quad (6.6)$$

where K_{eq} is the equilibrium constant.

If two or more ions react to form a solid precipitate and the reaction is reversible, then it can be represented as



The equilibrium relationship of this reaction is:

$$K_{sp} = \frac{[A]^a [B]^b}{[AB]^c} \quad (6.8)$$

where K_{sp} is called a **solubility product**. The activity of the solid together with the water is defined as unity. Solubility products can be used to compute the concentration

of a solute in equilibrium with a solid phase, either via dissolution of the solid into an undersaturated solution or following precipitation of the solid from a saturated solution.

If one is dealing with a very dilute aqueous solution, then molal concentrations can be used to determine chemical equilibrium. However, for the general case, one must use **chemical activities** to employ the law of mass action.

The chemical activity of ion X, [X], is equal to the molal concentration of X, m_x , times a factor known as an **activity coefficient**, γ_x :

$$[X] = m_x \gamma_x \quad (6.9)$$

A. Chemical activity (see above)

B. Affinity

AFFINITY

Establishing whether a chemical reaction such as the halite dissolution reaction will actually take place is accomplished by comparing the composition of the solution to the value of the equilibrium constant using the following expression:

$$A = R \times T \times \ln \left(\frac{Q}{K} \right) \quad (5.6)$$

where:

A is called the affinity (J/mole)

R is the universal gas constant (8.314 J/mole-K)

T is the temperature (K)

Q is the activity quotient for the relevant species in the applicable reaction

K is the equilibrium constant for that same reaction

If the measured solution composition results in an activity product that is equal to K , the affinity will be 0, indicating that the solution is in equilibrium with the solids, and no net dissolution or precipitation will occur. If the affinity were greater than 0, the concentration of the solutes exceeds the equilibrium value and the solution would begin to precipitate solid. This situation is one in which the solution is *supersaturated* in the solid involved in the reaction. For affinities less than 0, the reactant (in this case, our halite solid phase) would continue to dissolve until it is completely dissolved or the activity product of the solutes becomes equal to K , and equilibrium would be achieved.

This situation with respect to the values of affinity suggests that, mathematically, A must be equivalent to the Gibbs energy function of a reaction as indicated in Equation 3.16 (given below)

$$A = G_{\text{products}} - G_{\text{reactants}} = (H_{\text{products}} - H_{\text{reactants}}) - T \times (S_{\text{products}} - S_{\text{reactants}})$$

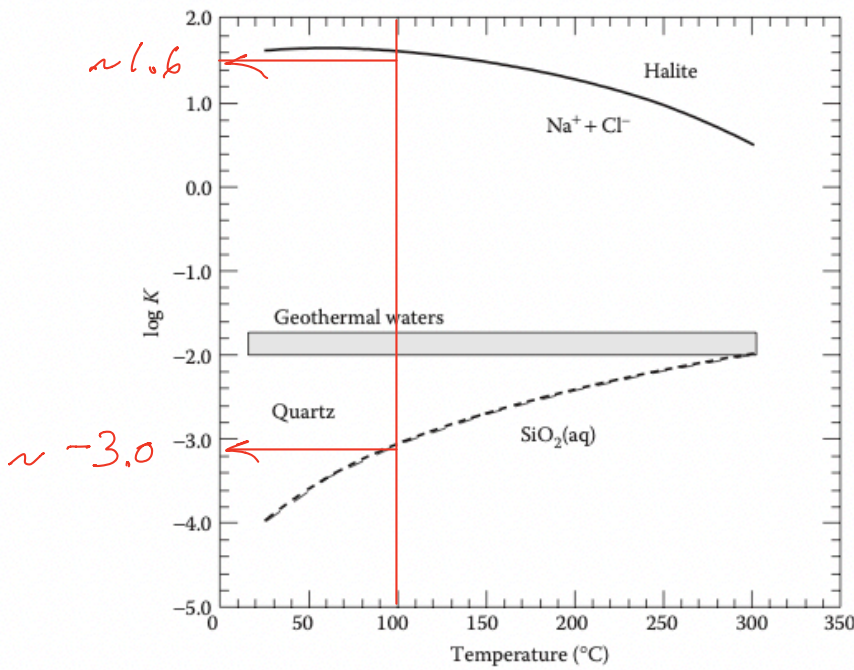
This relationship leads to the fundamental expression

$$\Delta G = -R \times T \times \ln(K) \quad (5.7)$$

which is a statement of the relationship between the activities of the species involved in a reaction and the conditions under which they will coexist in thermodynamic equilibrium.

At 100°C, the value for $\log K$ for the halite dissolution reaction is about 1.6 (Figure 5.2). On a molar basis, and assuming ideal behavior of the ions in solution, this means that a little more than 6 moles, each, of Na^+ and Cl^- must be dissolved in solution to achieve saturation. Given that the molecular weight of sodium is about 22.99 g/mole and that of Cl is about 35.39 g/mole, the respective masses of Na and Cl in a saturated solution will be a little more than 145 g and 220 g. Clearly, our original 10 g of salt added to the pan would completely dissolve, the solution would remain strongly undersaturated, and the resulting affinity and Gibbs energy would be much less than zero.

For the quartz in the pot, the situation is different. The value for K at 100°C is about 0.001 (Figure 5.2), which translates into a total SiO_2 (aq) concentration of about 0.06 g at equilibrium, or approximately 60 parts per million. Clearly, in this case, we have added to the pot of water much more quartz than would ever dissolve. In fact, so little would dissolve that it would not be noticeable unless we carefully weighed it before and after our experiment. In other words, quartz has a low *solubility* under these conditions.



$$\log K = 1.6$$

$$K = 10^{1.6} \sim 40.$$

$$\log K = -3$$

$$K \sim 0.001$$

FIGURE 5.2 Variation of the equilibrium constant for halite and quartz dissolution, as a function of temperature. The gray box encloses the range of aqueous SiO₂ compositions for the geothermal waters listed in Table 5.1.

4. Solubility

10g of NaCl @ 100°C $\log K = 1.6$
 $K = 40$

$$[Na][Cl] = 40 \quad \therefore \sim \sqrt{40} \sim 6 \text{ moles}$$

$$\left. \begin{array}{l} Na : 23 \text{g/mole} \times 6 \sim 150 \text{g} \\ Cl : 35 \text{g/mole} \times 6 \sim 210 \text{g} \end{array} \right\} \text{ saturation}$$

10g in 1 liter \therefore undersaturated

10g of SiO₂ @ 100°C $\log K = -3$
 $K \sim 0.001$

$$[SiO_2] = 0.001$$

$$\left. \begin{array}{l} Si : 28 \text{g/mole} \\ O : 16 \text{g/mole} \times 2 \end{array} \right\} \sim 60 \text{g/mole}$$

$$60 \text{ g/mole} \times 0.001 \sim 0.6 \text{ g}$$

@ saturation

\therefore 10g is much more than would dissolve.

Consequences of Affinity and Gibbs Energy

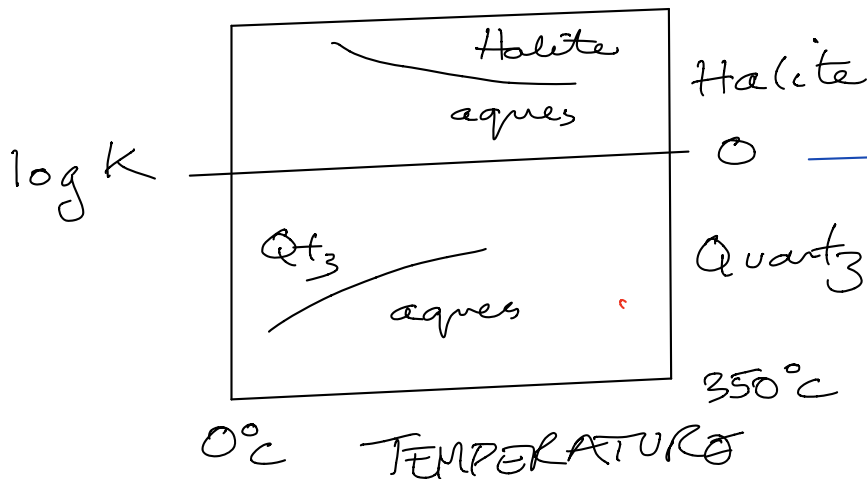
$$\Delta G = -R \times T \times \ln(K)$$

\uparrow
+ve (8.314 J/m.K)

log K (+ve)

\therefore ΔG and Affinity (-ve)

Undersaturated



log K (-ve)

\therefore ΔG and Affinity

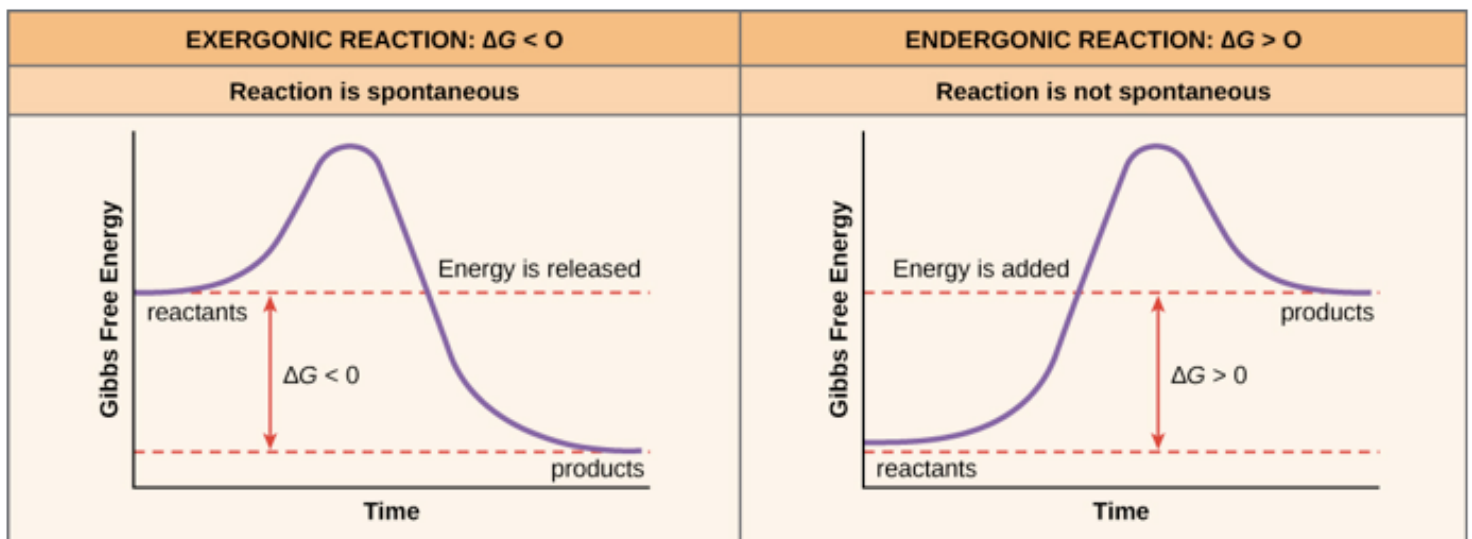
(+ve)

Saturated

RELEVANCE OF GIBBS ENERGY

$$\underline{\Delta G = \Delta H - T \Delta S}$$

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	Spontaneous at all T ($\Delta G < 0$)	Spontaneous at high T (when $T\Delta S$ is large)
$\Delta S < 0$	Spontaneous at low T (when $T\Delta S$ is small)	Non-spontaneous at all T ($\Delta G > 0$)



PROGRADE VS RETROGRADE SOLUBILITY

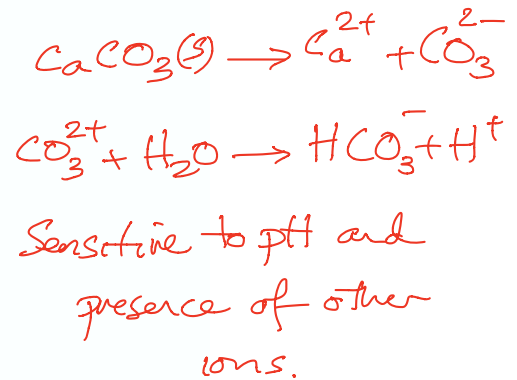
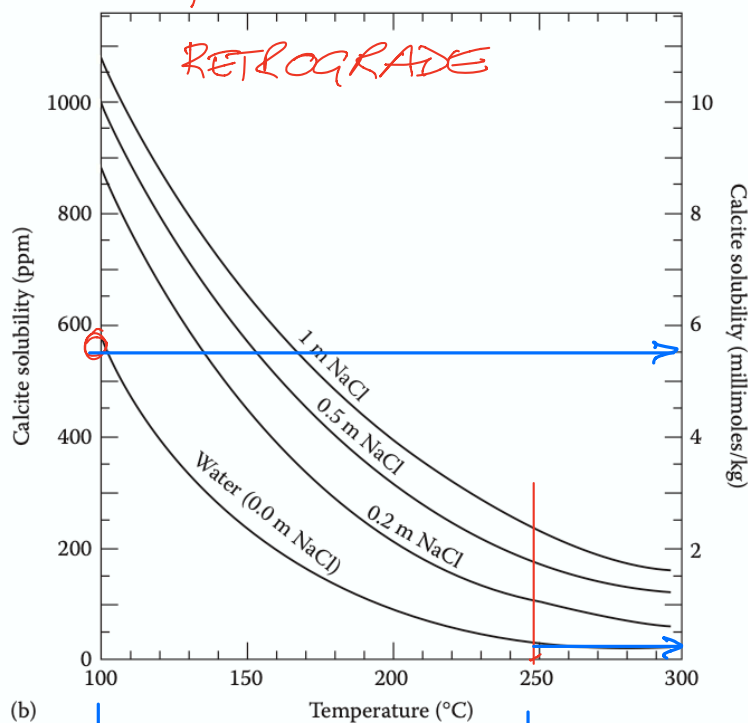
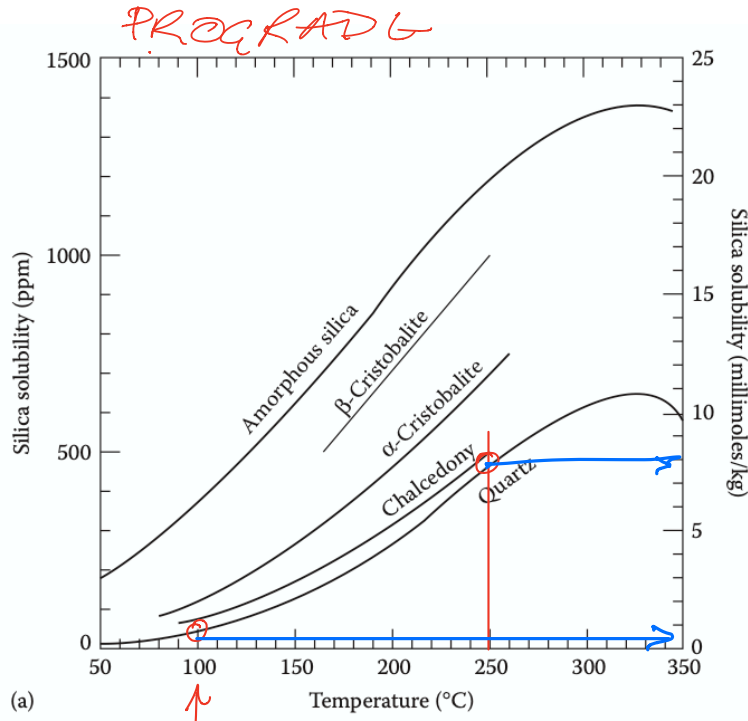


FIGURE 5.3 Comparison of the solubility of (a) quartz and (b) calcite, as a function of temperature and composition of the solvent (for calcite).

↓ 100°C ↓ 250°C

←

← Saturated

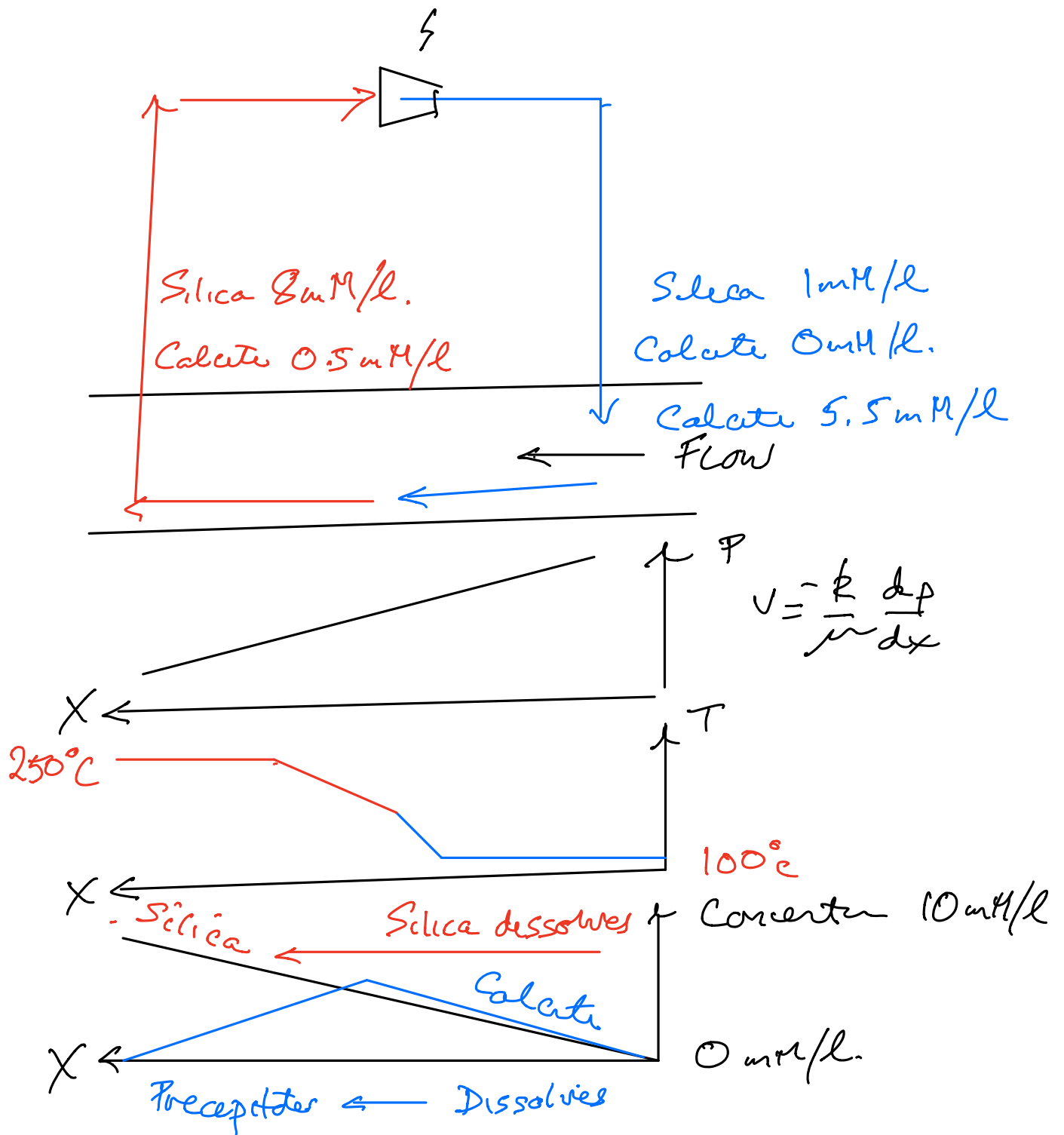
Precipitation
Dissolution

< 1 mM
5.5 mM

~ 8 mM/liter Silica

< 0.5 mM/liter Calcite

IMPLICATIONS OF DISSOLUTION/PRECIPITATION



[3:3] Mass Transport

Recap $\underline{S} \dot{\underline{c}} + [\underline{K}_d + \underline{K}_a] \underline{c} = \underline{q} + \underline{R}$

Reactive transport

Sorption

First-order reactions

Multiple reactions

Reaction Rates

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}) - \nabla \cdot (D_i \nabla c_i) = R_i \quad (1)$$

For the reaction:



$$\text{Forward rate} = k_1[A][B]$$

$$\text{Reverse rate} = k_2[C] \quad (3)$$

At equilibrium:

$$\text{Forward rate} = \text{Reverse rate}$$

$$k_1[A][B] = k_2[C] \quad (4)$$

$$\therefore [A][B] = \frac{k_2}{k_1}[C] \quad (5)$$

For closed system and one mole each of [A] and of [B], with $k_1 = 1$ and $k_2 = 10$, then:

$$\frac{[A][B]}{[C]} = \frac{(1-X)^2}{X} = \frac{10}{1} \quad (6)$$

And $(1-X) = [A] = [B] = 0.916$ and $X=[C] = 0.0839$.

Implementation:

$$\begin{aligned} R_A &= -k_1[A][B] + k_2[C] \\ R_B &= -k_1[A][B] + k_2[C] \\ R_C &= +k_1[A][B] - k_2[C] \end{aligned} \quad (7)$$

Generalized:

$$R_i = -k_i^f \prod_{j=1}^N [c_j^f]^{\alpha_j^f} + k_i^r \prod_{j=1}^N [c_j^r]^{\alpha_j^r} \quad (8)$$

Heats of reaction:

$$H_i = R_i \Delta H_i \quad (9)$$

And heat balance requires:

$$\rho c \frac{\partial T}{\partial t} + \nabla \cdot (T \mathbf{u}) - \nabla \cdot (\lambda \nabla T) = H_i \quad (10)$$

REACTION RATES

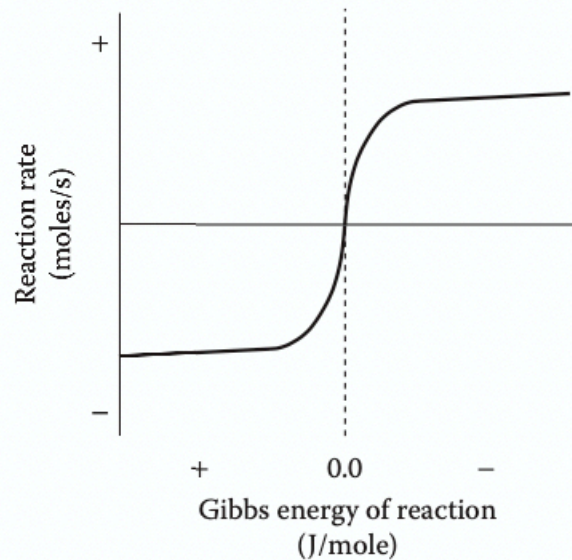


FIGURE 5.5 Variation of the reaction rate plotted as a function of the Gibbs energy of a reaction.

Graphically, this relationship appears as shown in Figure 5.5. Hence, any equation describing this behavior must be able to account for the far-from-equilibrium behavior as well as the behavior close to equilibrium.

One such general reaction rate equation, written in a form that uses the measured dissolution rate for reference, is given by

$$R = S_A \times k \times T_{\text{fac}} \times \alpha \times \phi \times \prod a_i \times \left(\frac{1-Q}{K} \right)^\omega \quad (5.8)$$

where:

R is the rate (moles/s)

S_A is the effective surface area exposed to the fluid (cm^2)

k is the far-from-equilibrium rate constant ($\text{moles}/\text{cm}^2\text{-s}$)

T_{fac} is the temperature correction factor for the rate constant k (usually an Arrhenius function)

α is a power function that accounts for changes in the rate close to equilibrium conditions

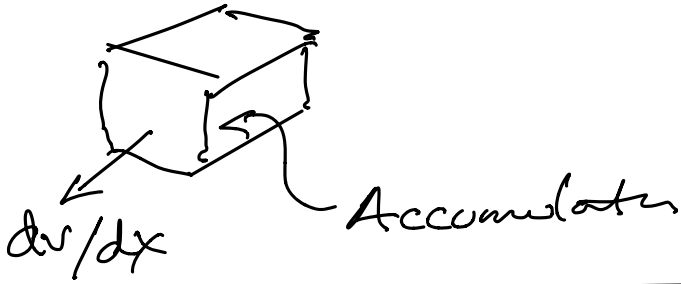
ϕ is a function that modifies the rate for precipitation relative to that for dissolution

a_i accounts for the dependence of the rate on the activities of specific components in solution (often this is mainly a reflection of the activity of the hydrogen ion, H^+)

Q/K is the same as in Equation 5.6

ω is the power dependence that accounts for the particular dissolution or precipitation mechanism (for details see discussions in the works of Lasaga et al. [1994] and Glassley et al. [2003])

CONSERVATION RELATIONS



$$\frac{\partial \rho}{\partial t} + \rho \frac{\partial v}{\partial x} = 0$$

MASS

WATER FLOW - Conserve fluid mass

$$\text{Darcy's law } v_d = -\frac{k}{\mu} \frac{dp}{dx}$$

$$\text{Compressibility } C = \frac{1}{\rho} \frac{\partial \rho}{\partial p}$$

$$C \frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left(-\frac{k}{\mu} \frac{\partial p}{\partial x} \right) = q_f$$

SOLUTE FLOW - Conserve mass of solute

$$\text{Fick's Second law } v_{di} = -D \frac{\partial^2 c}{\partial x^2}$$

$$\text{Advective flux } v_d = v_f c$$

$$\frac{\partial c}{\partial t} + v_f \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} = R$$

HEAT FLOW - Conserve thermal energy, U

$$\text{Fourier's law } v_{th} = -k \frac{\partial T}{\partial x}$$

$$\text{Advective flux } v_{th} = v_f \rho c T$$

$$\left((1-\phi) \rho c_m + \phi \rho c_w \right) \frac{\partial T}{\partial t} + \rho c_w v \frac{\partial T}{\partial x} - k \frac{\partial^2 T}{\partial x^2} = q_{th}$$

SIMILAR EQUATIONS

$$A \frac{\partial T}{\partial t} + B \frac{\partial T}{\partial x} + C \frac{\partial^2 T}{\partial x^2} = D$$

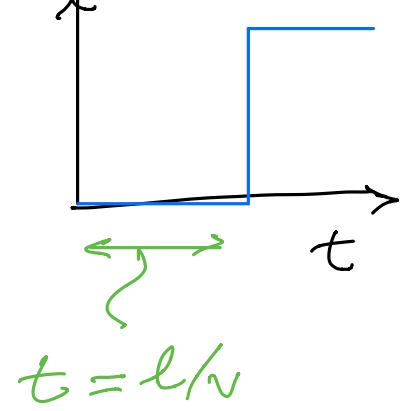
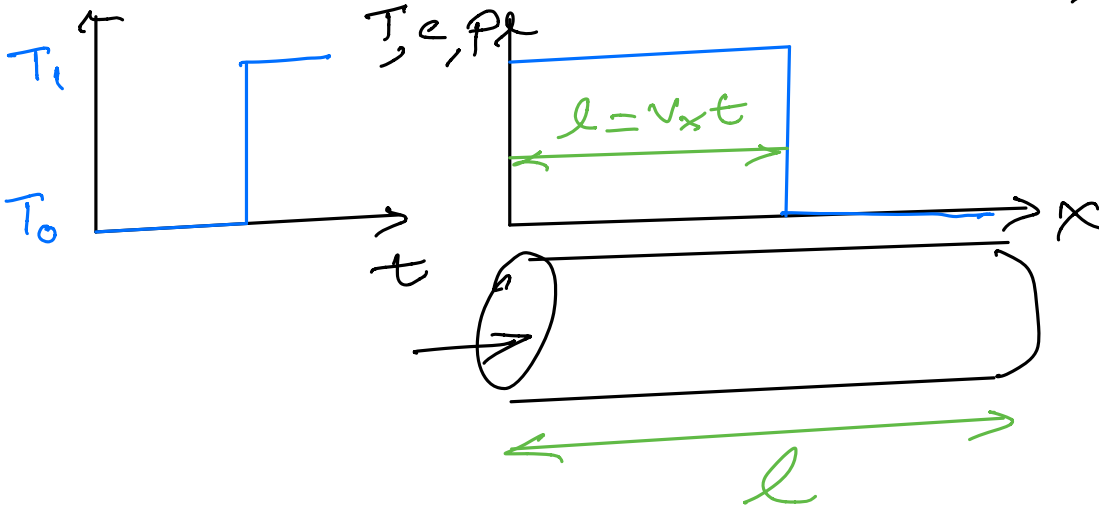
Accumulate

Advection

Diffusion

SIMILAR SOLUTIONS

T, C, P



APPROACHES TO REACTIVE TRANSPORT MODELING

1. Pseudo-reactive using linear isotherms

- Retardation approach \rightarrow gives chromatographic effect
- Adsorption of monolayer of components at sorption sites
- No pore clogging or dissolution
- Multi-component retardation possible, but no reaction/interaction

2. First order reaction with a single component

- Reaction rate law defines rate of precipitation/dissolution
- Dissolution/precipitation may be used to update pore volume/surface area/permeability

3. Reaction with multiple reacting components

- Complex interacting solutes
- Precipitation/dissolution

General approaches of 2. & 3.

1. Determine $\partial c/\partial t$ in transport (spatial)
2. Determine $\partial c/\partial t$ in species due to reaction.



PSEUDO-REACTIVE SYSTEM

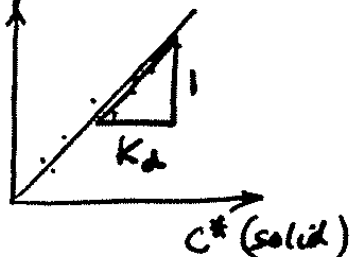
"RETARDATION" APPROACH

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{v_d}{n} \frac{\partial c}{\partial x} - \frac{\rho_b}{n} \frac{\partial c^*}{\partial t}$$

concentration on mineral surfaces

$$\frac{\partial c^*}{\partial t} = \frac{\partial c^*}{\partial c} \frac{\partial c}{\partial t} \Rightarrow K_d \frac{\partial c}{\partial t}$$

Linear isotherm:
(Aqueous) c

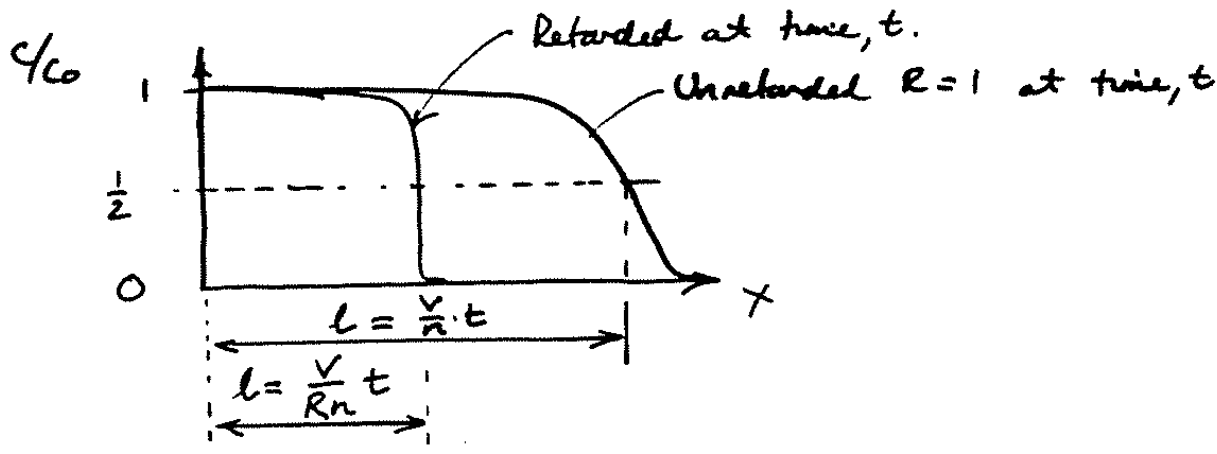


Replacing $\frac{\rho_b}{n} \frac{\partial c^*}{\partial t}$ yields a modified transport equation

$$\left(1 + \frac{\rho_b}{n} K_d\right) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{v_x}{n} \frac{\partial c}{\partial x}$$

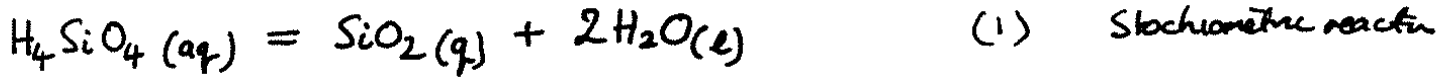
R = retardation coefficient

$$\frac{\partial c}{\partial t} = \frac{D}{R} \frac{\partial^2 c}{\partial x^2} - \frac{v_x}{Rn} \frac{\partial c}{\partial x}$$



FIRST ORDER REACTION - SINGLE COMPONENT

Dissolution/Precipitation of Quartz



$$\left(\frac{\partial c}{\partial t}\right)_{\text{Rxn}} = -k(c - c_{\text{eq}}) \quad (2) \quad \text{Rate law}$$

↑
equilibrium concentration - no precip./dissol.

Transport Equation (one component) for fluid phase.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{v_x}{n} \frac{\partial c}{\partial x} + \left(\frac{\partial c}{\partial t}\right)_{\text{Rxn}}$$

Translate to FE statement:

$$\int_V \underline{b}^T \underline{b} \, dV \underline{c} + D \int_V \underline{a}^T \underline{a} \, dV \underline{c} + \frac{v_x}{n} \int_V \underline{b}^T \underline{a} \, dV \underline{c} - k_1 \int_V \underline{b}^T \underline{b} \, dV (\underline{c} - \underline{c}_{\text{eq}}) = \underline{q}$$

$$\underline{K}_0 \dot{\underline{c}} + D \underline{K}_{\text{II}} \underline{c} + \frac{v_x}{n} \underline{K}_{\text{I}} \underline{c} - k_1 \underline{K}_0 (\underline{c} - \underline{c}_{\text{eq}}) = \underline{q}$$

Separate terms for solution (implicit time stepping ($\Delta t=1$)):

$$\left[\frac{1}{\Delta t} \underline{K}_0 + D \underline{K}_{\text{II}} + \frac{v_x}{n} \underline{K}_{\text{I}} - k_1 \underline{K}_0 \right] \underline{c}^{t+\Delta t} = \underline{q}^{t+\Delta t} + \frac{1}{\Delta t} \underline{K}_0 \underline{c}^t$$

Mass Accumulation + Diffusion + Advection + Dissol./Precip - $k_1 \underline{K}_0 \underline{c}^t$

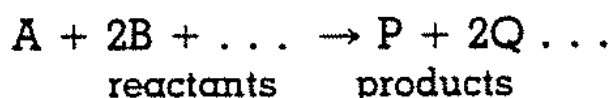
Solve for \underline{c} with time

These are fluid concentrations of any species (quartz)

Similar to retardation approach.

2.4. THE RATE LAW

We can show experimentally that for the general irreversible reaction



we can write the rate law,

$$\frac{d[\text{A}]}{dt} = -k[\text{A}]^{\alpha}[\text{B}]^{\beta}[\text{P}]^{\rho}[\text{Q}]^{\sigma} \dots \quad (2-1)$$

where

$$\frac{d[\text{A}]}{dt} = \text{time rate of change in molar concentration of species A,}$$

k = reaction rate constant, and

$\alpha, \beta, \rho, \sigma, \dots$ = constants

In this book, [] is used to signify concentration in moles/liter. We may use concentration units other than moles/liter in the rate law but in doing so we should use the same concentration unit for each species and realize that both the numerical value and units of the reaction rate constant will differ from those found when molecular concentrations are used.

Using our knowledge of the stoichiometry of the reaction, that is, the relative number of moles of species reacting and the relative number of moles of products being formed as the reaction proceeds, we can state that

$$\frac{d[\text{A}]}{dt} = \frac{1}{2} \frac{d[\text{B}]}{dt} \dots = \frac{-d[\text{P}]}{dt} = \frac{-1}{2} \frac{d[\text{Q}]}{dt} \dots \quad (2-2)$$

because 1 mole of A reacts for every 2 moles of B that react, and so forth, and 1 mole of P is formed for every mole of A that reacts, and so forth. We can determine the reaction order from the rate law. The overall reaction order is

$$\alpha + \beta + \rho + \sigma \dots \quad (2-3)$$

while the order with respect to A is α , the order with respect to B is β , and so forth. If the reaction is irreversible, then ρ, σ, \dots , the exponents of the product concentration, are usually zero. For example, if

$$\frac{d[\text{A}]}{dt} = -k[\text{A}][\text{B}]^2$$

then we would say that the reaction was first order with respect to A, second order with respect to B, and third order overall. It is important to note that reaction order is generally not determined by the stoichiometry of the overall reaction. Laboratory experimentation is necessary to determine the order.

The following example illustrates several points that are important for a good understanding of the rate law.

Integrated forms of the rate law are very useful for analyzing rate data to determine reaction rate constants and reaction order. Let us first consider the irreversible reaction



which has the rate law

$$\frac{d[A]}{dt} = -k[A]^n$$

To determine the behavior of $[A]$ as a function of time, we must integrate the rate expression with respect to time. We will do this for several values of the reaction order, n . When $n = 0$, the reaction is zero order, and

$$\frac{d[A]}{dt} = -k[A]^0 = -k \quad (2-4)$$

Upon integrating, we obtain

$$[A] = [A]_0 - kt \quad (2-5)$$

where $[A]_0$ = the concentration of A at $t = 0$, that is, the initial concentration of A . The *half-life*, $t_{1/2}$, or time for 50 percent of the initial concentration to react can be obtained from Eq. 2-5 by setting $[A] = 0.5 [A]_0$ when $t = t_{1/2}$. Then

$$t_{1/2} = \frac{0.5[A]_0}{k}$$

When $n = 1$, the reaction is *first order*, both with respect to A and overall, and we can write,

$$\frac{d[A]}{dt} = -k[A] \quad (2-6)$$

Rearranging Eq. 2-6 and solving the integral,

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = - \int_0^t k dt$$

we find

$$\ln [A] = \ln [A]_0 - kt \quad (2-7)$$

or

$$[A] = [A]_0 e^{-kt} \quad (2-8)$$

Examination of Eq. 2-7 suggests that the rate constant k may be determined experimentally from a plot of $\ln [A]$ versus t , which has a slope of $-k$. Also, from Eq. 2-8, when $[A] = 0.5 [A]_0$, we find the half-life to be

$$t_{1/2} = \frac{0.693}{k}$$

If the reaction is greater than first order, then we can write

$$\frac{d[A]}{dt} = -k[A]^n \quad (2-9)$$

PROCESS COUPLINGS [T-H-M-C]

$$\begin{bmatrix} \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & R_{42} & \dots & R_{44} \\ \dots & \dots & \dots & \dots \end{bmatrix} \begin{Bmatrix} \underline{u} \\ \underline{p} \\ \underline{T} \\ \underline{c} \end{Bmatrix} + \begin{bmatrix} \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & S_{44} \end{bmatrix} \begin{Bmatrix} \underline{\dot{u}} \\ \underline{\dot{p}} \\ \underline{\dot{T}} \\ \underline{\dot{c}} \end{Bmatrix} = \begin{Bmatrix} \underline{f} + \dots \\ \underline{q}_F + \dots \\ \underline{q}_T + \dots \\ \underline{q}_M + \dots \end{Bmatrix}$$

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c}{\partial x^2} - \frac{v_x}{n} \frac{\partial c}{\partial x} + \left(\frac{\partial c_i}{\partial t} \right)_{R \times N}$$

Reaction with Multiple Reacting Components

See for example: Steefel & MacQuarrie in "Reactive Transport in Porous Media"
Ed. Lichtner, P.C., Steefel, C.I. and Oelkers, E.H.
Mineralogical Soc. of Amer. 1996.

Basic Approach

1. Write a single equation for each species considered, as:

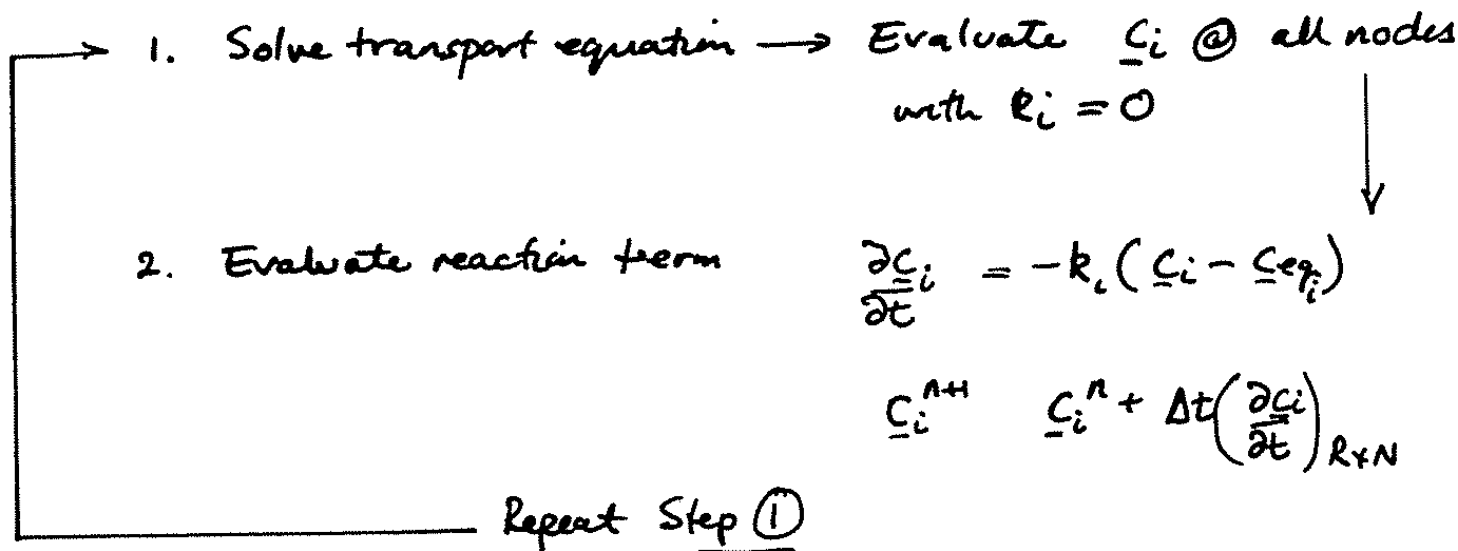
$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - \frac{v_x}{n} \frac{\partial c_i}{\partial x} + R_i c_i$$

$$\text{Reaction rate: } R_i c_i = \frac{\partial c_i}{\partial t} = -k_i (c - c_{eq})$$

$$\approx \frac{\partial c_i}{\partial t} = -k_i [c]$$

Components are not necessarily independent

2. Solve sequentially as:



REACTION ALGORITHMS FOR MULTICOMPONENT SYSTEMS

Mathematical descriptions of reaction systems

The multicomponent, multi-species systems typical of those which occur in porous media require some special treatment, both because they involve multiple unknowns and because they are usually nonlinear. The mathematical description used, however, will depend on what form the reactions in the system are assumed to take. It is instructive to derive a general approach to handle multicomponent, multi-species reactive systems. Formulations for arbitrarily complex reaction systems characterized by both equilibrium and non-equilibrium reactions have been presented by Lichtner (1985), Lichtner (this volume), Friedly and Rubin (1992), Sevougian et al. (1993), and Chilakapati (1995). A clear discussion of one possible way of doing so is given by Chilakapati (1995). His approach begins with the most general case, a set of ordinary differential equations for each species in the system and reactions between the species described by kinetic rate laws. A system containing N_{tot} species and N_r reactions can be expressed as

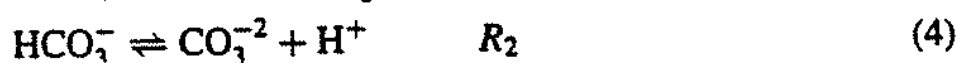
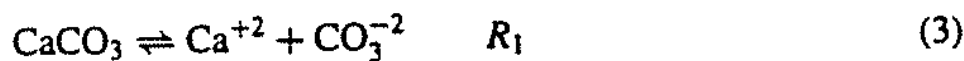
$$\mathbf{I} \cdot \frac{d\mathbf{C}}{dt} = \nu \cdot \mathbf{R} \quad (1)$$

The raised dot indicates matrix multiplication. \mathbf{I} is the identity matrix of dimension $N_{tot} \times N_{tot}$, \mathbf{C} is the vector of solute concentrations of length N_{tot} , ν is a matrix of dimension $N_{tot} \times N_r$, and \mathbf{R} is a vector of length N_r . For example, the matrix ν and the vector \mathbf{R} have the form

$$\nu = \begin{bmatrix} \nu_{1,1} & \nu_{1,2} & \cdots & \nu_{1,N_r} \\ \nu_{2,1} & \nu_{2,2} & \cdots & \nu_{2,N_r} \\ \vdots & \cdots & \cdots & \vdots \\ \nu_{N_{tot},1} & \nu_{N_{tot},2} & \cdots & \nu_{N_{tot},N_r} \end{bmatrix} \quad \mathbf{R} = \begin{bmatrix} R_1 \\ R_2 \\ \cdots \\ R_{N_r} \end{bmatrix} \quad (2)$$

The multiplication of the identity matrix by the derivatives of the individual species concentrations results in an ODE of similar form for each of the species in the system.

As an example, consider an aqueous system consisting of Ca^{+2} , H^+ , OH^- , CO_3^{-2} , HCO_3^- , H_2CO_3 , and $\text{CaCO}_3(\text{s})$ (calcite). We ignore H_2O for the sake of conciseness. In addition, we assume that the following reactions occur, without yet specifying whether they are to be considered equilibrium or kinetically-controlled reactions,



In the above equations R_i symbolizes the rate expression for reaction i . We also make no assumptions at this stage about whether the set of reactions included are linearly independent (although the reactions listed above are). We have shown the reactions to be reversible here (thus the symbol \rightleftharpoons) but the results below apply whether the reactions are irreversible or reversible since at this stage, one can think of the reaction rates as simply time-dependent expressions of the mole balances inherent in a balanced chemical reaction. The reversibility or lack thereof only determines whether the sign of the reaction rate can change. The term *reversible* is generally used by thermodynamicists to refer to equilibrium reactions (Lichtner, this volume), although we prefer to use it to refer to reactions which are sufficiently close to equilibrium that the backward reaction is important. It is quite possible in a steady-state flow system, for example, for backward reactions to be important and yet not to be at equilibrium (e.g. Nagy et

al., 1991; Nagy and Lasaga, 1992; Burch et al., 1993). According to this definition, the term *irreversible* is used for those reactions which proceed in only one direction (i.e. those that can be represented with a unidirectional arrow, \longrightarrow).

For our example aqueous system, the rates for the individual species can be written

$$\frac{d[\text{H}_2\text{CO}_3]}{dt} = -R_3 \quad (7)$$

$$\frac{d[\text{HCO}_3^-]}{dt} = -R_2 \quad (8)$$

$$\frac{d[\text{CaCO}_3]}{dt} = -R_1 \quad (9)$$

$$\frac{d[\text{OH}^-]}{dt} = -R_4 \quad (10)$$

$$\frac{d[\text{H}^+]}{dt} = R_2 + 2R_3 - R_4 \quad (11)$$

$$\frac{d[\text{Ca}^{+2}]}{dt} = R_1 \quad (12)$$

$$\frac{d[\text{CO}_3^{-2}]}{dt} = R_1 + R_2 + R_3. \quad (13)$$

In matrix form the system of equations becomes

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{d[\text{H}_2\text{CO}_3]}{dt} \\ \frac{d[\text{HCO}_3^-]}{dt} \\ \frac{d[\text{CaCO}_3]}{dt} \\ \frac{d[\text{OH}^-]}{dt} \\ \frac{d[\text{H}^+]}{dt} \\ \frac{d[\text{Ca}^{+2}]}{dt} \\ \frac{d[\text{CO}_3^{-2}]}{dt} \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 1 & 2 & -1 \\ 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \\ R_3 \\ R_4 \end{bmatrix} \quad (14)$$

As written in Equation (14), the stoichiometric reaction matrix, ν , is referred to as being in *canonical* form (Smith and Missen, 1982; Lichtner, 1985; Lichtner, this volume). The system of equations is partitioned into the first four rows where the associated species (H_2CO_3 , HCO_3^- , $\text{CaCO}_3(\text{s})$, and OH^-) are involved in only one reaction while in the remaining three rows the species are involved in multiple reactions. The first four species are referred to as secondary or non-component species, while the last three are the primary or component species (Lichtner, this volume). These are also referred to as *basis* species because they form a basis which spans the concentration space. In this example, we have written all of the carbonate reactions using the species CO_3^{-2} precisely so as to restrict all of the other carbonate species to involvement in a single reaction. This is an essential first step in obtaining either the canonical formulation (Lichtner, 1985; Lichtner, this volume) or to writing the reactions in *tableaux* form (Morel and Hering, 1993), both of which assume that one is dealing with a set of linearly independent reactions, but it is not essential for what follows below. The procedure will also work if, for example, the formation of H_2CO_3 involved H^+ and HCO_3^- rather than 2H^+ and CO_3^{-2} , although we will not obtain the conserved quantities (total H^+ , total CO_3^{-2} , etc.) found in the tableaux method without additional manipulations.

The system of ODEs could be solved directly in the form of Equation (14) if the reactions are all described with kinetic rate laws. Alternatively, one can apply a Gauss-Jordan elimination

process to the matrix ν and simultaneously to the identity matrix \mathbf{I} until there are no pivots left (Chilakapati, 1995). The resulting transformed set of ODEs is now

$$\mathbf{M} \cdot \frac{d\mathbf{C}}{dt} = \nu^* \cdot \mathbf{R} \quad (15)$$

which partitions the system of equations into N_r ODEs associated with reactions and N_c conservation laws with zero right-hand sides (i.e. no associated reactions). The number of conservation laws or mole balance equations is equal to

$$N_c = N_{tot} - \text{rank of } \nu = N_{tot} - N_r. \quad (16)$$

N_r , therefore, refers to the number of *linearly independent* reactions between the species in the system. For the sake of clarity, we make the first N_r rows of the matrix \mathbf{M} the ODEs with associated reactions and the next N_c rows the conservation equations, so that the left hand of Equation (15) takes the form

$$\begin{bmatrix} M_{1,1} & \cdots & M_{1,N_r+N_c} \\ \vdots & \cdots & \vdots \\ M_{N_r,1} & \cdots & M_{N_r,N_r+N_c} \\ M_{N_r+1,1} & \cdots & M_{N_r+1,N_r} \\ \vdots & \cdots & \vdots \\ M_{N_r+N_c,1} & \cdots & M_{N_r+N_c,N_r+N_c} \end{bmatrix} \cdot \begin{bmatrix} \frac{dC_1}{dt} \\ \vdots \\ \frac{dC_{N_r}}{dt} \\ \vdots \\ \frac{dC_{N_r+N_c}}{dt} \end{bmatrix} \quad (17)$$

In our example, the Gauss-Jordan elimination is carried out on the the matrix ν on the right hand side of Equation (14) and the same row transformations are applied to the identity matrix, \mathbf{I} , yielding

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 1 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{d[\text{H}_2\text{CO}_3]}{dt} \\ \frac{d[\text{HCO}_3^-]}{dt} \\ \frac{d[\text{CaCO}_3]}{dt} \\ \frac{d[\text{OH}^-]}{dt} \\ \frac{d[\text{H}^+]}{dt} \\ \frac{d[\text{Ca}^{+2}]}{dt} \\ \frac{d[\text{CO}_3^{2-}]}{dt} \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \\ R_3 \\ R_4 \end{bmatrix} \quad (18)$$

The stoichiometric reaction matrix, ν^* , now consists of a nonsingular 4 by 4 matrix (N_r by N_r) and three rows of zeros corresponding to the N_c conservation equations. Writing out the ODEs in Equation (18), we find

$$\frac{d[\text{H}_2\text{CO}_3]}{dt} = -R_3 \quad (19)$$

$$\frac{d[\text{HCO}_3^-]}{dt} = -R_2 \quad (20)$$

$$\frac{d[\text{CaCO}_3]}{dt} = -R_1 \quad (21)$$

$$\frac{d[\text{OH}^-]}{dt} = -R_4 \quad (22)$$

Table 1. Tableaux for carbonate system, neglecting H₂O as a species and component.

		Components		
		H ⁺	Ca ⁺²	CO ₃ ⁻²
Species	H ₂ CO ₃	2		1
	HCO ₃ ⁻	1		1
	CaCO ₃		1	1
	OH ⁻	-1		
	H ⁺	1		
	Ca ⁺²		1	
	CO ₃ ⁻²			1

and

$$\frac{d}{dt} ([H^+] + 2[H_2CO_3] + [HCO_3^-] - [OH^-]) = 0 \quad (23)$$

$$\frac{d}{dt} ([Ca^{+2}] + [CaCO_3]) = 0 \quad (24)$$

$$\frac{d}{dt} ([CO_3^{-2}] + [H_2CO_3] + [HCO_3^-] + [CaCO_3]) = 0. \quad (25)$$

From the example, it is apparent that we have eliminated the reactions in the equations originally corresponding to the species H⁺, Ca⁺², and CO₃⁻² by making use of the relations in the first four equations. The last three equations are mole balances for *total* H⁺, Ca⁺², and CO₃⁻²

$$TOT_{H^+} = [H^+] - [OH^-] + [HCO_3^-] + 2[H_2CO_3] \quad (26)$$

$$TOT_{Ca^{+2}} = [Ca^{+2}] + [CaCO_3] \quad (27)$$

$$TOT_{CO_3^{-2}} = [CO_3^{-2}] + [H_2CO_3] + [HCO_3^-] + [CaCO_3]. \quad (28)$$

Note that the canonical form of the stoichiometric reaction matrix is identical to the *tableaux* form popularized by Morel and coworkers (Morel and Hering, 1993; Dzombak and Morel, 1990). By transposing the last three rows of the matrix **M** in Equation (17), we can write the matrix in tableaux form (Table 1).

The procedure has yielded expressions for the total concentrations of the *N_c primary or component* species. A more general form is given by

$$TOT_j = C_j + \sum_{i=1}^{N_r} \nu_{ij} X_i \quad (29)$$

where *C_j* and *X_i* refer to the concentration of the primary and secondary species respectively. Note that the number of secondary species is equal to *N_r*, the number of linearly independent reactions in the system (i.e. the rank of the matrix *ν*). Equation (27) and Equation (28) are recognizable as the total concentrations of calcium and carbonate respectively. The total concentration of H⁺ is written in exactly the same form as the other equations, although its physical meaning is less clear because it may take on negative values due to the negative stoichiometric coefficients in the expression. The mole balance equation for total H⁺ is just the *proton condition* equation referred to in many aquatic chemistry textbooks. Oxidation-reduction reactions are also easily handled with this method. If the redox reactions are written as whole cell reactions, there is no need in any application not involving an electrical current (see Lichtner, this volume) to introduce the electron as an unknown. Writing the reactions as whole cell reactions allows redox reactions to be treated exactly like any other reaction.

CONVECTIVE HEAT FLOW

Assume - Thermal equilibrium of fluid and rock $\therefore T_R = T_F$
and only 1 variable

- Not necessary to make this assumption (convenient).

$$D^* \frac{\partial^2 T}{\partial x^2} - \rho_f c_f q_b \frac{\partial T}{\partial x} = (\bar{\rho}c) \frac{\partial T}{\partial t}$$

$\rho_f c_f n + (1-n)\rho_r c_r$

$D^* = D_r(1-n) + D_f(n)$ Darcy flux $q_b = -\frac{k}{\mu} \frac{dp}{dx}$

FE Equations:

$$D^* \frac{\partial^2 T}{\partial x^2} = D^* \int_V \underline{a}^T \underline{a} \, dV \, \underline{T} = \underline{K}_2 \underline{T}$$

$$\rho_f c_f q_b \frac{\partial T}{\partial x} = \rho_f c_f q_b \int_V \underline{b}^T \underline{a} \, dV \, \underline{T} = \underline{K}_1 \underline{T}$$

$$\bar{\rho}c \frac{\partial T}{\partial t} = \bar{\rho}c \int_V \underline{b}^T \underline{b} \, dV \, \dot{\underline{T}} = \underline{K}_0 \dot{\underline{T}}$$

ASSEMBLED EQUATIONS: (Implicit, $\lambda=1$)

$$[\underline{K}_2 + \underline{K}_1] \underline{T}^{t+\Delta t} + \underline{K}_0 \dot{\underline{T}}^{t+\Delta t} = \underline{q}_f^{t+\Delta t}$$

$\dot{\underline{T}} = \frac{1}{\Delta t} [\underline{T}^{t+\Delta t} - \underline{T}^t]$

GATHERING TERMS:

$$[\underline{K}_2 + \underline{K}_1 + \frac{1}{\Delta t} \underline{K}_0] \underline{T}^{t+\Delta t} = \underline{q}_f^{t+\Delta t} + \frac{1}{\Delta t} \underline{K}_0 \underline{T}^t$$

may change if q_b changes in time.

SYSTEM TYPES

SOLID MECHANICS

- Conservation of momentum:
(Equilibrium), $\nabla \cdot \underline{T} = \underline{W}_E$
- Continuity (Compatibility):
 $\underline{\underline{\epsilon}} = \underline{\underline{a}} \underline{\underline{u}}$
- Constitutive relation: $\underline{\underline{\sigma}} = \underline{\underline{D}} \underline{\underline{\epsilon}}$
- Initial Conditions
- Boundary Conditions

FLOW SYSTEM

- Conservation of mass:
 $\nabla \cdot \underline{\underline{q}} = 0$
- Continuity: $\underline{\underline{h}}_t = \underline{\underline{a}} \underline{\underline{h}}$
- Constitutive reln. $\underline{\underline{v}} = \underline{\underline{D}} \underline{\underline{h}}$
- ICs
- BCs

TRANSPORT

- Conservation of mass
 $\nabla \cdot \underline{\underline{q}} = 0$
- Continuity: $\underline{\underline{c}}_t = \underline{\underline{a}} \underline{\underline{c}}$
- Constitutive:
diffusion - $\underline{\underline{v}}_1 = \underline{\underline{D}} \underline{\underline{c}}$,
advective - $\underline{\underline{v}}_2 = \underline{\underline{A}} \underline{\underline{c}}$
- ICs
- BCs

- SOLVE SYSTEM EQUATIONS -

6. Reservoir/Plan response - Sauty (1980) and EnvSE 408 Section 3.2