CHEMICAL REACTIONS AND DIFFUSION

A.K.A. "NETWORK THERMODYNAMICS"

BACKGROUND

“Classical” thermodynamics describes equilibrium states.

Non-equilibrium thermodynamics describes steady states.

“Network thermodynamics” describes dynamics.
**Simple Substance:**

Using molar units for mass (units of $N$: e.g., Kg-moles, pound-moles)

$$U = U(S,V,N)$$

**Variable mass makes this a 3-port capacitor**

Generalized displacement associated with mass variation (i.e., the “mass flow port”):

- Mass, $N$
- Corresponding flow variable: mass flow rate, $\frac{dN}{dt} = \dot{N}$
- Corresponding effort variable: evaluate total differential

$$dU = (\frac{\partial U}{\partial S})dS + (\frac{\partial U}{\partial V})dV + (\frac{\partial U}{\partial N})dN$$

$$dU = TdS - PdV + \mu dN$$

$$\mu \Delta \frac{\partial U}{\partial N} \Bigg|_{S,V}$$

Remember that the mass flow and entropy flow ports are coupled.
**Multi-component system:**

Applies to reactions, diffusion, phase changes, etc.

\[ U = U(S,V,m_1,...m_n) \]

Rewrite in terms of moles using \( m_i = M_i N_i \) where \( N_i \) are numbers of moles and \( M_i \) are molecular weights.

\[ U = U(S,V,N_1, ...N_n) \]

This describes a multi-port capacitor with a port for each mass variable.

For each distinct component, define a distinct effort.

\[ \text{d}U = T\text{d}S - P\text{d}V + \sum_i \mu_i \text{d}N_i \]

\[ \mu_i \Delta \left. \frac{\partial U}{\partial N_i} \right|_{S,V} \]
Typical boundary conditions: constant temperature and pressure.

The corresponding co-energy function is the Gibbs function.

\[ G = U - TS + PV = G(P, T, N_1, ..., N_n) \]

\[ dG = dU - TdS - SdT + PdV + VdP \]

\[ dG = \sum \mu_i dN_i - SdT + VdP \]

Hence the effort variable is chemical potential

Gibbs free energy per mole.

Aside:

\[ \frac{\partial G}{\partial N_i} \bigg|_{P, T} = \frac{\partial U}{\partial N_i} \bigg|_{S, V} \]
CAPACITOR CONSTITUTIVE EQUATIONS

In general, the constitutive equations of this multi-port capacitor are coupled

\[ \mu_i = \mu_i(N_1, \ldots, N_n, T, P) \]

In some simple cases, the constitutive equations are uncoupled.

In most of what follows, for clarity we will ignore the temperature and pressure ports.

EXAMPLE: IDEAL GAS MIXTURE

Constitutive equation for each ideal component of a mixture of ideal gases

(valid for dilute solutions, low pressure gas mixtures)

\[ \mu_i(T, P_i) = \mu_i(T, P) + RT \ln(P_i/P) \]

where

- \( P_i \) is the partial pressure of constituent \( i \),
- \( P \) and \( T \) are the pressure and temperature of the mixture (usually assumed constant),
- \( R \) is the universal gas constant.
Rewrite using *mole fractions* $y_i$ of the constituents (which determine the composition of the mixture)

$$P_i / P = N_i / N = y_i$$

where

$$N = \sum_i N_i$$ is the total number of moles in the mixture.

$$\mu_i = \mu_i^\circ + RT \ln y_i$$

where $\mu_i^\circ = \mu_i(T,P)$ is the reference chemical potential.

**In general the total number of moles need not be constant.**

If so, the constitutive equation is that of a coupled multi-port capacitor.

$$\mu_i = \mu_i(N_1, \ldots N_n).$$

(The pressure and temperature ports have been neglected for simplicity.)

To simplify we will consider only reactions for which $N$ is constant.

**Constitutive equations are then those of n uncoupled one-port capacitors**

$$\mu_i = \mu_i(N_i)$$
**General reaction:**

The relative magnitudes of the molar flows of the constituents are constrained by the reaction. Analogous to a kinematic constraint

**Stoichiometric coefficients describe the constraint.**

Reactants \( \nu_R S_1 + \nu_R S_2 + \ldots \) \( \Leftrightarrow \) Products \( \nu_P S_1 + \nu_P S_2 + \ldots \)

\( S_i \) denotes species \( i \)

\( \nu \) subscript \( R \) denotes reactants

\( P \) denotes products.

**Example:**

\( 2 \text{H}_2 + \text{O}_2 \Leftrightarrow 2 \text{H}_2\text{O} \)

**Define a stoichiometric coefficient for species \( i \)**

\( \nu_i = \nu_{Pi} - \nu_{Ri} \)

**General equations describing progress or advancement of the reaction in terms of mole numbers are:**

\( N_i(t) = N_i(0) + \nu_i \xi(t) \)

\( \xi(t) \) is an advancement coordinate

where \( \xi(0) = 0 \)
Example:

\[ A + B \iff 2 \cdot D \]

\[ 1 \cdot A + 1 \cdot B + 0 \cdot D \iff 0 \cdot A + 0 \cdot B + 2 \cdot D \]

Stoichiometric coefficients:

- \( \nu_{RA} = 1; \ \nu_{RB} = 1; \ \nu_{RD} = 0 \]

- \( \nu_{PA} = 0; \ \nu_{PB} = 0; \ \nu_{PD} = 2 \]

- \( \nu_A = -1; \ \nu_B = -1; \ \nu_D = 2 \)

The time variation of numbers of moles of the various species are related as follows:

\[
N_A(t) = N_A(0) - \xi(t)
\]

\[
N_B(t) = N_B(0) - \xi(t)
\]

\[
N_D(t) = N_D(0) + 2 \xi(t)
\]

where \( \xi(0) = 0 \).

In general the total number of moles may vary.

\[
N(t) = \sum_i N_i(t) = N(0) + \nu \xi(t)
\]

where \( \nu = \sum_i \nu_i = \sum_i \nu_{Pi} - \sum_i \nu_{Pi} \)

In the following we will assume that \( \nu = 0 \) and the total number of moles is constant.
AFFINITIES:

The advancement coordinate plays the role of a displacement.

The corresponding effort is an affinity:

\[
\frac{\partial G}{\partial N_i} \, dN_i = \sum_i \mu_i \, dN_i = d\xi \sum_i \mu_i \, v_i
\]

\[
dG_{P,T} = d\xi \sum_i \mu_i (v_{P_i} - v_{R_i}) = d\xi \left( \sum_i \mu_i v_{P_i} - \sum_i \mu_i v_{R_i} \right)
\]

Definitions:

Forward affinity: \( A_F = \sum_i \mu_i v_{R_i} \)

Reverse affinity: \( A_R = \sum_i \mu_i v_{P_i} \)

Affinity:

\( A = A_F - A_R \)

Thus

\( dG = -A \, d\xi \)

Note that affinity is an effort in the usual sense.

Just like force, \( A \) is the negative gradient of a (co-)energy function.

At equilibrium, \( dG = 0 \) and \( A = 0 \) or \( A_F = A_R \).
Meaning of variables

\( N_i \) is mass (in moles)
\( \dot{N}_i \) is a mass flow rate (moles/sec)
\( \dot{\xi} \) is also a mass flow rate
\( \dot{\mu}_i N_i \) is a power flow
\( A \dot{\xi} \) is also a power flow

**Example:**

\[ A + B \rightarrow 2D \]

\( A_F = \mu_A + \mu_B \quad A_R = 2 \mu_D \)

Equilibrium \quad \( A_F = A_R \quad \mu_A + \mu_B = 2 \mu_D \)

This reaction may be depicted as follows

\[ \begin{align*}
A & \xrightarrow{\mu_A} 0 \xrightarrow{\dot{N}_A} TF / \nu_A \\
B & \xrightarrow{\mu_B} 0 \xrightarrow{-\dot{N}_B} TF / \nu_B
\end{align*} \]

\[ \begin{align*}
A_F & \xleftarrow{\dot{\xi}} TF / \nu_A \\
A_R & \xrightarrow{\dot{\xi}} TF / \nu_D \xrightarrow{\mu_D} C:D
\end{align*} \]

The stochiometric coefficients are represented as the moduli of transformers.
CHANGE OF VARIABLES:

If total number of moles is constant, we may describe reaction advancement in terms of mole fractions

\[ y_{Si}(t) = y_{Si}(0) + v_i x(t) \]

The dimensionless number \( x(t) = \frac{\xi(t)}{N} \) is termed the degree of reaction.

The time variation of mole fractions of the various species are related as follows

\[ y_A(t) = y_A(0) - x(t) \]
\[ y_B(t) = y_B(0) - x(t) \]
\[ y_D(t) = y_D(0) + 2 x(t) \]

where \( x(0) = 0 \)
This change of variables may be depicted as follows.

\[ \begin{align*}
\text{A} + \text{C} & \xrightarrow{\mu_{A}} \frac{\text{TF}}{\bar{N}_A} \\
\bar{N}_A & \xrightarrow{\dot{y}_A} \dot{x} \\
\text{B} + \text{C} & \xrightarrow{\mu_{B}} \frac{\text{TF}}{\bar{N}_B} \\
\bar{N}_B & \xrightarrow{\dot{y}_B} \\
\end{align*} \]

Note:

It has been implicitly assumed that the affinities are scaled by the total number of moles.
REACTION KINETICS

Aside:
The following results are usually derived from kinetic theory. This alternative derivation is fully equivalent.

So far we have described equilibrium energy storage. There is, as yet, no representation of the process.

The process will be represented by a dissipative element.

Consider an even simpler two-component reaction

\[
\begin{align*}
A &\rightleftharpoons B \\
\text{A:} &\quad \text{C:} \\
\text{A} &\quad \text{B} \\
\end{align*}
\]

\[
\begin{align*}
A_F &= \mu_A \\
A_R &= \mu_B \\
A &= \mu_A - \mu_B \\
-\dot{y}_A &= \dot{x} = \dot{y}_B \\
\end{align*}
\]
To formulate dynamic equations for a state determined system we need rate to be a function of state.

Consider $\dot{x} = g(A)$

$$\dot{x} = g\left[ (\mu_A^\circ - \mu_B^\circ) + RT \ln(y_A/y_B) \right]$$

If so, the rate of advancement depends only on the *ratio* of number of moles

e.g., double both of the mole fractions (or concentrations) and the advancement rate is unchanged.

In general, this is only valid near equilibrium.

Typically, doubling both of the concentrations will double the reaction rate.
POINT:

A one-port resistor cannot describe reaction rates far from equilibrium.

That requires a coupled 2-port resistor with constitutive equation $\dot{x} = g(A_F, A_R)$.

This general relation describes many different models of reaction kinetics, including the law of “mass action”.
LAW OF “MASS ACTION”

Net reaction rate is proportional to the product of mole fractions (concentrations) of reactants and products.

Alternatively, net reaction rate is the difference between a forward reaction rate

— proportional to the product of reactant mole fractions

and a reverse reaction rate

— proportional to the product of product mole fractions

In general

$$\dot{x} = k_F \prod_{i} y_i^{v_{Ri}} - k_R \prod_{i} y_i^{v_{Pi}}$$

$k_F$ and $k_R$ are forward and reverse reaction rate constants.
At equilibrium, the rate of reaction advancement is zero (forward and reverse reaction rates balance)

The reaction rate constants are related as follows

\[ \dot{x} = 0 \]

\[ k_F \prod_{i} y_i^{*v_{Ri}} = k_R \prod_{i} y_i^{*v_{Pi}} \]

\[ \frac{k_F}{k_R} = \frac{\prod_{i} y_i^{*v_{Pi}}}{\prod_{i} y_i^{*v_{Ri}}} = \prod_{i} y_i^{*(v_{Pi} - v_{Ri})} = \prod_{i} y_i^{*v_i} \]

The asterisk denotes equilibrium.

The equilibrium constant of the reaction is

\[ \kappa = \frac{k_F}{k_R} = \prod_{i} y_i^{*v_i} \]

It depends only on temperature.
ASIDE:

In general the equilibrium product of mole fractions depends on temperature and pressure.

Strictly speaking, the equilibrium constant that is independent of temperature is defined in terms of partial pressures as

$$\prod_{i}(P_i^*/P)^{\nu_i} = \kappa(T)$$

If the total number of moles may vary and $\nu \neq 0$, the equilibrium product of mole fractions is different from the equilibrium product of partial pressures as follows.

$$\prod_{i}y_i^{\nu_i} = (P^\circ/P)^{\nu} \prod_{i}(P_i^*/P)^{\nu_i} = (P^\circ/P)^{\nu} \kappa(T)$$

where $P^\circ$ denotes a reference pressure.

If the total number of moles is constant, $\nu = 0$ and the two constants are identical.
Example:

For the simple reaction $A \Leftrightarrow B$

$$\dot{x} = k_F y_A - k_R y_B$$

Using the definition of the rate of advancement for this reaction we obtain two coupled first-order differential equations describing the time variation of the composition (mole fractions) of the mixture.

$$\dot{x} = \dot{y}_B = k_F y_A - k_R y_B$$
$$\dot{x} = -\dot{y}_A = k_F y_A - k_R y_B$$

The equilibrium constant is defined by $\dot{x} = 0$

$$\kappa = \frac{k_F}{k_R} = \frac{y_B^*}{y_A^*}$$
Using the constitutive equations of the capacitors we may relate the equilibrium constant to the equilibrium chemical potentials and the net change of Gibbs free energy at equilibrium.

At equilibrium $\mu_A^* = \mu_B^*$
(asterisk denotes equilibrium)

\[
\therefore \mu_A^\circ - \mu_B^\circ = RT \ln \left( \frac{y_B^*}{y_A^*} \right)
\]

\[
\kappa(T) = \frac{y_B^*}{y_A^*} = \exp \left( \frac{\mu_A^\circ - \mu_B^\circ}{RT} \right) = \exp \left( -\frac{\Delta G^\circ}{RT} \right)
\]

where $-\Delta G^\circ = \mu_A^\circ - \mu_B^\circ$

The constitutive equation for the 2-port dissipator is

\[
\dot{x} = k_F e^{-\mu_A^\circ/RT} \left( e^{A_F/RT} - e^{A_R/RT} \right) = -\dot{y}_A = \dot{y}_B
\]

Thus the simple two-component reaction may be depicted as follows.
EXAMPLE:

Reconsider the reaction $A + B \Leftrightarrow 2 \text{D}$

Law of mass action:

\[
\dot{x} = k_F y_A y_B - k_R y_D^2
\]

at equilibrium

\[
\dot{x} = 0
\]

\[
\therefore k_F y_A^* y_B^* = k_R y_D^{*2}
\]

\[
\mu_A^* + \mu_B^* = 2 \mu_D^*
\]

\[
\therefore \mu_A^0 + \mu_B^0 - 2 \mu_D^0 = RT \ln \left( \frac{y_D^{*2}}{y_A^* y_B^*} \right)
\]

\[
\kappa(T) = \frac{k_F}{k_R} = \frac{y_D^{*2}}{y_A^* y_B^*} = \exp \left( \frac{-\Delta G^0}{RT} \right)
\]

where $-\Delta G^0 = \mu_A^0 + \mu_B^0 - 2 \mu_D^0$
Substitute for $y_A$, $y_B$ and $y_D$ in the law of mass action using the capacitor constitutive equations

\[
y_A = \exp\left(\frac{\mu_A - \mu_A^\circ}{RT}\right)
\]
\[
y_B = \exp\left(\frac{\mu_B - \mu_B^\circ}{RT}\right)
\]
\[
y_D = \exp\left(\frac{\mu_D - \mu_D^\circ}{RT}\right)
\]

we may define the temperature-dependent constant

\[
G = k_F \exp\left(-\frac{(\mu_A^\circ + \mu_B^\circ)}{RT}\right) = k_R \exp\left(-\frac{2\mu_D^\circ}{RT}\right)
\]
The constitutive equations for the 2-port R and the associated junction structure are

\[ \dot{x} = G \left( e^{A_F/RT} - e^{A_R/RT} \right) = -\dot{y}_A = -\dot{y}_B = 2 \dot{y}_D \]

The reaction may be depicted as follows.

![Diagram of reaction pathway]
Are we justified in treating the reaction kinetics as a two-port resistor?

If so, the net power into the resistor must be positive definite.

\[ P_{\text{net,in}} = P_{\text{in}} - P_{\text{out}} = A_F \dot{x} - A_R \dot{x} = A \dot{x} \]

by definition, \( G > 0 \)

if \( A_F > A_R \) then \( e^{A_F/RT} > e^{A_R/RT} \) and \( \dot{x} > 0 \)

if \( A_F < A_R \) then \( e^{A_F/RT} < e^{A_R/RT} \) and \( \dot{x} < 0 \)

if \( A_F = A_R \) then \( e^{A_F/RT} = e^{A_R/RT} \) and \( \dot{x} = 0 \)

\[ \therefore A \dot{x} \geq 0 \]

The law of mass action does, indeed, describe a dissipator, a 2-port resistor.
ONSGER RECIPROCITY

For convenience, temporarily change notation so that power is positive into both ports of the 2-port R.

\[ \dot{x} = -\dot{z} \]

Now linearize

\[
\frac{\partial \dot{x}}{\partial A_F} = \frac{G}{RT} e^{A_F/RT} \frac{e^{A_F/RT}}{RT} = -\frac{\partial \dot{z}}{\partial A_F},
\]

\[
\frac{\partial \dot{x}}{\partial A_R} = \frac{G}{RT} e^{A_R/RT} = -\frac{\partial \dot{z}}{\partial A_R},
\]

\[
\begin{bmatrix}
\dot{x} \\
\dot{z}
\end{bmatrix} =
\begin{bmatrix}
\frac{G}{RT} e^{A_F/RT} & -\frac{G}{RT} e^{A_F/RT} \\
\frac{G}{RT} e^{A_R/RT} & \frac{G}{RT} e^{A_R/RT}
\end{bmatrix}
\begin{bmatrix}
A_F \\
A_R
\end{bmatrix}.
\]
This is a conductance matrix. 

\[
\begin{bmatrix}
\dot{x} \\
\dot{z}
\end{bmatrix} = \begin{bmatrix} Y & A_F \\
A_R & \end{bmatrix}
\]

\( Y \) is non-negative definite

As above, \( A\dot{x} \geq 0 \)

\( Y \) is singular because \( \dot{x} = -\dot{z} \)

The constraint on the flows may *look like* a zero junction

but the constitutive equations determining the flows cannot (in general) be expressed as function of effort differences

In general, this is *not* a nodic 2-port.

Now consider equilibrium

\( A_{F^*} = A_{R^*} \)

\( Y \) becomes symmetric.

Symmetry of the conductance matrix at equilibrium is known as *Onsager reciprocity*. 

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At (or near) equilibrium, the law of mass action may be represented by the one-port resistor and the one junction above.

The 1-port $R$ constitutive equation is

$$ \dot{x} \approx \frac{G}{RT} \exp(\frac{AF^*/RT}{}}$$

However, far from equilibrium, $Y$ is not symmetric. Thus the 2-port $R$ contains an “embedded gyrator”

Reaction kinetics are closely analogous to transistor behavior.

In fact, transistor circuits may be used to model complex reactions.
Diffusion (e.g. across a membrane) may be treated exactly like a reaction

\[ A \rightleftharpoons A^\bullet \]

In that “reaction” the total number of moles is constant.

\[ \nu = 0 \]

\[ k_F = k_R = p \text{ (permeability)} \]

The equilibrium constant is

\[ \kappa = \frac{k_F}{k_R} = 1 \]