Lecture 5.1

Thermodynamics of Reactions

O'Connell & Haile
Chapter 7.4-7.7

Topics:

- Formulation of reactions:
  - Species, independent reactions
- Extent of reaction & stoichiometric coefficients
- Affinity
- Laws of Thermodynamics for reactions
- Reaction equilibrium

REACTING SYSTEMS

For species *i* made from elements *k* (from 1 to m_e) with formula a_{ki}, conservation of elements yields

$$\sum_i^C a_{ki} N_i = b_k \quad 1, 2, \ldots, m_e \qquad \textbf{(7.4.1)}$$

Matrix form, AN=b,

- A = nonsquare coefficient array
- N = vector of length *C*,
- b = vector of length m_e

Closed system $\sum_i^C a_{ki} dN_i = 0 \quad 1, 2, \ldots, m_e$ **(7.4.3)**

Could guess reactions, but better to get from A

independent reactions, *R*, from *Rank* of A

$$R = C - Rank\ (\mathbf{A}) \qquad \textbf{(7.4.5)}$$

See Appendix B for linear algebra

Extent of reaction, ξ_j, stoichiometric coefficient, ν_{ij} defined relative to reference species (7.4.7)-(7.4.12)

$$N_i = N_i^0 + \sum_{j=1}^R \nu_{ij} \xi_j \quad i = 1, 2. \ldots, C \qquad \textbf{(7.4.13)}$$

Change in number of moles of species *i*

$$dN_i = \sum_{j=1}^R \nu_{ij} d\xi_j \quad i = 1, 2. \ldots, C \qquad \textbf{(7.4.15)}$$

With eq 7.4.3, $\sum_j^R \left(\sum_{i=1}^C a_{ki} \nu_{ij} \right) d\xi_j = 0 \quad k = 1, 2, \ldots, m_e$

giving $\mathbf{A}\underline{\nu}_j = \underline{0} \quad j = 1, 2, \ldots, R \qquad \textbf{(7.4.17)}$

Mole fractions from definition, (7.4.19)-(7.4.21)

$$x_i = \frac{N_i}{\sum_m^C N_m} = \frac{N_i}{N} = \frac{N_i^0 + \sum_j^R \nu_{ij} \xi_j}{N^0 + \sum_j^R \sigma_j \xi_j} \qquad \textbf{(7.4.22)}$$

where $\sigma_j \equiv \sum_i^C \nu_{ij} \quad j = 1, 2, \ldots, R$

Note upper bound on ξ_j from stoichiometry with limiting reactant going to zero

But never reached because of equilibrium

COMMENTS ABOUT EXTENTS OF REACTION

Stoichiometric coefficients determined only to a factor; if all ν_{ij} multiplied by constant, OK

Only need single variable, ξ_j, for each reaction to get all species moles, mole fractions,

Value of ξ_j depends on ν_{ij} chosen; bounds vary

ξ_j is extensive, expect to be +, but need not be
Range from 0 to value when limiting reactant disappears or equilibrium reached.

MULTIPLE REACTIONS

A matrix gives *R*, find ν_j by solving

$$\mathbf{A}\nu_j = \underline{0} \text{ with } \nu_{1j} = -1$$

Examine Synthesis Gas Example 7.4.3

LAWS FOR REACTING SYSTEMS

Change of reaction in property F* by reaction *j

$$\Delta F_j \equiv \sum_i^C \nu_{ij} \overline{F}_i \qquad \textbf{(7.4.40)}$$

Affinity from change of Gibbs energy, reaction *j*

$$\mathcal{A}_j \equiv -\Delta G_j = -\sum_i^C \nu_{ij} \overline{G}_i \quad j = 1, 2, \ldots, R \qquad \textbf{(7.4.41)}$$

Using Gibbs-Duhem Equation on property *F*

$$dF = \left.\frac{\partial F}{\partial T}\right|_{PN} dT + \left.\frac{\partial F}{\partial P}\right|_{TN} dP + \sum_j^R \Delta F_j d\xi_j \qquad \textbf{(7.4.44)}$$

If *F* = *G*, finally get (7.4.49) $\sum_j^R \mathcal{A}_j \nu_j \geq 0$ **(*T*,*P* fixed)**

Single / uncoupled reaction(s) proceed ($\nu_j > 0$) for $\mathcal{A}_j > 0$

Coupled reactions must use constraint of whole sum >0; common in living systems

Glucose / Urea Example

$2NH_3 + CO_2 = (NH_2)_2CO + H_2O$ $\quad \mathcal{A}_1 = -46$ kJ mol^{-1}

$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$ $\quad \mathcal{A}_2 = 482$ kJ mol^{-1}

Allows $0 < \nu_1 < \frac{482}{46} \nu_2 > 0$

Section 7.5 - Open systems
7.5.1 gives MB for species (not conserved)

$$\sum_\alpha \dot{N}_i^\alpha - \sum_\beta \dot{N}_i^\beta + \sum_j \nu_{ij} \nu_j = \dot{N}_i^{acc} \qquad \textbf{(7.5.4)}$$

Multiple phases & reactions, get general relation
Heat / work / diffusion terms in (7.2.13) + reaction

$$\delta Q^{\beta}\left(\frac{T^{\alpha}}{T^{\beta}}-1\right)-(\delta W^{\alpha}+\delta W^{\beta})-$$
$$\sum_{i=1}^{C}\left[\overline{G}_i^{\alpha}-\left(\overline{H}_i^{\beta}-T^{\alpha}\overline{S}_i^{\beta}\right)\right]dN_i^{\alpha,dif}$$
$$\sum_{k=1}^{R}\left[\mathcal{A}_k{}^{\alpha}d\xi_k^{\alpha}-\sum_{i=1}^{C}\left(\overline{H}_i^{\beta}-T^{\alpha}\overline{S}_i^{\beta}\right)\nu_{ij}d\xi_k^{\alpha}\geq 0\right. \quad \textbf{(7.5.10)}$$

For $T^{\alpha}=T^{\beta},\ \overline{H}_i^{\beta}-T^{\alpha}\overline{S}_i^{\beta}=\overline{G}_i^{\beta},\ \sum_{i=1}^{C}\left(\overline{H}_i^{\beta}-T^{\alpha}\overline{S}_i^{\beta}\right)\nu_{ij}=\mathcal{A}_k{}^{\beta}$

Allows for diffusion / reaction coupling

$$-\sum_{i=1}^{C}\left(\overline{G}_i^{\alpha}-\overline{G}_i^{\beta}\right)\ +\ (\mathcal{A}_k{}^{\alpha}d\xi_k^{\alpha}-\mathcal{A}_k{}^{\beta}d\xi_k^{\beta})\geq 0 \quad \textbf{(7.5.11)}$$

REACTION EQUILIBRIUM

Closed & Open Systems, no reaction when

$$\sum_{j}^{R}\mathcal{A}_j\nu_j = 0 \qquad (T,\ P \text{ fixed}) \qquad \textbf{(7.6.1)}$$

Note same as *dG* = 0 in example 7.6.3
Equilibria if $\nu_j = 0$ & $\mathcal{A}_j = 0$, uncouples reactions

Metastability if $\nu_j = 0$ but $\mathcal{A}_j \neq 0$
(Example: $H_2 + O_2 = 2H_2O$)

Calculations of <u>any</u> equilibrum / nonequilibrium system, use $\overline{G}_i(T,P,\{x\})$ or $f_i(T,P,\{x\})$ **for** $\mathcal{A}_j$
Can observe at equilibrium, probably not for nonequilibrium, so then must use models

In phase equilibrium, use fugacities directly

$$f_i'(T,P,\{x'\}) = f_i''(T,P,\{x''\})$$

In reaction equilibrium, use of fugacities complicated

$$\mathcal{A}_j(T,P,\{x\}) = -\sum_{i=1}^{C}\nu_{ij}\overline{G}_i(T,P,\{x\}) =$$

$$= -\sum_{i=1}^{C}\nu_{ij}\overline{G}_i^{0}(T,P,\{x\}) - \sum_{i=1}^{C}\nu_{ij}RT\ln\frac{f_i(T,P,\{x\})}{f_i^{0}(T,P^{0},\{x^{0}\})}$$

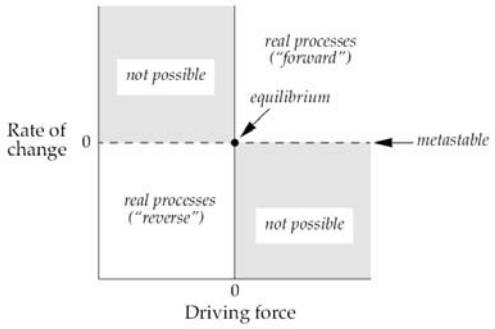
$$= \mathcal{A}_j{}^{0}(T,P^{0},\{x^{0}\}) - RT\ln\prod_{i=1}^{C}\left(\frac{f_i(T,P,\{x\})}{f_i^{0}(T,P^{0},\{x^{0}\})}\right)^{\nu_{ij}} \quad j=1,2,\ \ldots,R$$

Going forward to get *P*, {*x*}, use modeled f_i & f_i^0 as for phase equilibrium, but use <u>tabulated</u> information on $\mathcal{A}_j{}^{o} = \Delta G_j^{0}(T)$

Information obtained by going backward from experimental *T*, *P*, {*x*} plus modeling for f_i & f_i^{o} at equilibrium or by computation

SUMMARY

Entropy generation describes <u>all</u> spontaneous changes: heat, work, diffusion, reaction
For multiple processes individual mechanisms can go in "opposite direction" if coupled)



Always true equation (7.7.1)
$\Sigma[(driving\ force)(rate\ of\ change)$

Note tendencies & limitations on heat & work flow & resulting equilibria related to measurables *T* & *P*.
For diffusion & reaction, limitations conceptuals $\overline{G}_i$ & f_i ; more difficult to "understand" & also to compute.