# STRUCTURES IN ENGINEERING THERMODYNAMICS

**With Gratitude to**
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**For Details See**
***Chemical Engineering Education*, 27**, 96 (1993)

## SOME BASICS

**Engineers Are Problem Solvers with Goal of Manipulating Nature**
**Problem Solvers Use 3 Components for Effectiveness**
- **Knowledge**
- **Experience**
- **Problem Solving Skills**

D.R. Woods

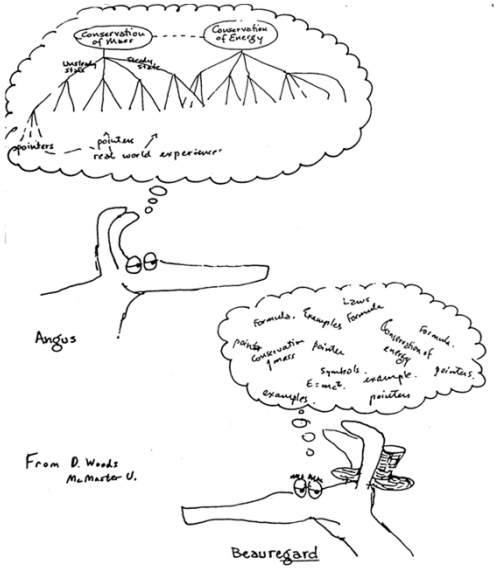
## MORE BASICS

**Knowledge Has Structure with Hierarchy**
- **Fundamentals Highest**
- **Applications Lowest**
- **Pointers Make Connections**

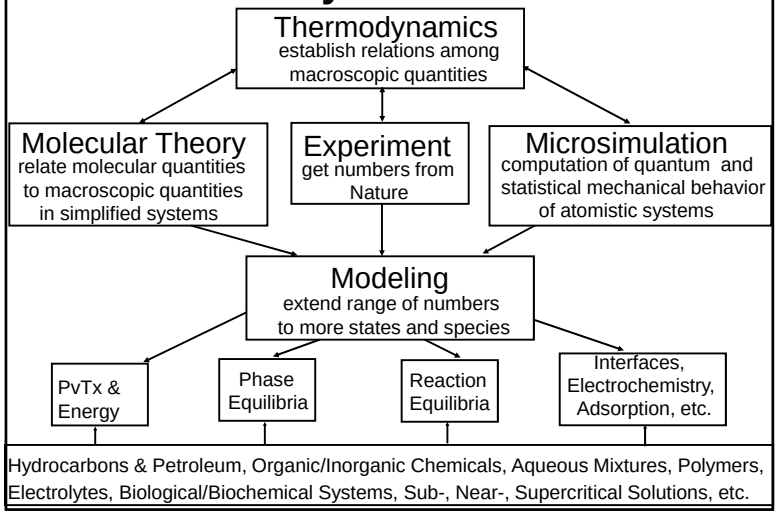
**Structure Evolves with Experience**

**Problem Solving Skills Use Efficient Structure**

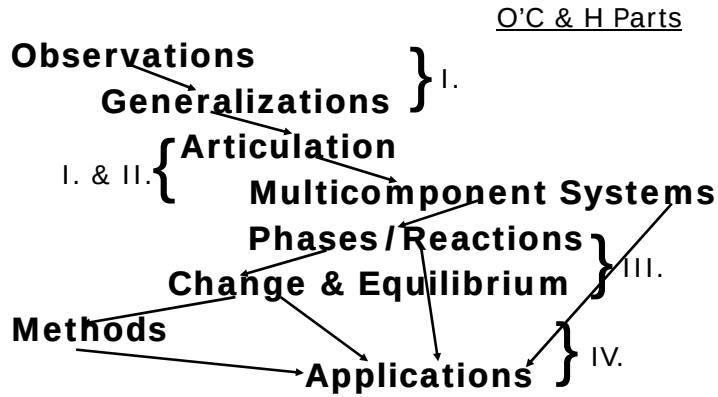
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## Structure of Chemical Engineering Thermodynamics Practice




## A STRUCTURE OF THERMODYNAMICS




Mostly Followed in O'Connell & Haile, "Thermodynamics: Fundamentals for Application", Cambridge, 2005

## OBSERVATIONS

**Primitive Concepts**

**MEASURABLES**

| Things | Properties | Changes |
|---|---|---|
| Mass | Force | Up & Down |
| Mixtures | Volume | In & Out |
| Phases | Temperature | Composition |

**Natural Phenomena**

**HAPPENINGS**

| | | |
|---|---|---|
| Thermal, Mechanical Effects on Fluids / Solids | Various Material Transfer Mechanisms | Chemical Reaction Regularities |

## GENERALIZATIONS I.

**(Primitives)**

| Definitions | Mathematics |
|---|---|
| Identity | Algebraic Equations |
| Chemical Species | Multivariable Functions |
| Interactions of System | Independent / Dependent |
| Quality | Variables |
| Extensive / Intensive | Calculus |
| Reversible / Irreversible | Derivatives / Integrals |
| Quantities | Differential Equations |
| Properties (*m*, *T*, *P*, . . .) | Exact / Inexact Differentials |
| Work | Path-Dependent Integration |
| Kinetic / Potential Energy | Balance Equations |

## GENERALIZATIONS II.
(Connections)

| Observations | Definitions | Equations |
|---|---|---|
| Mass Conserved (ex. Nuclear) | Atomic/Molecular "Weights" | Mass Balance $m_{in} - m_{out} = m_{acc}$ |
| # Independent Variables | Heat, Work & Material Interactions | (#Ind) = (#Work) + (#Species) + 1 = # Interactions |
| Connection of $P, V, T, x$ | Equation of State | $P = P(T, V, x)$<br>$V = V(T, P, N)$<br>$= Nv(T, P, x)$ |

## GENERALIZATIONS IIIA.
(The Laws)

**Work Is Path Dependent Except If No Thermal Interaction (Adiabatic)**

- Joule

**Closed System 1st Law Defines Energy, a Property, & Heat: Process-Dependent**

$\Delta E \equiv W_{adiabatic}$

$Q \equiv \Delta E - W$

**Energy Balance**

$E_{in}$ (*Work, Heat, Material*)
$- E_{out}$ (*Work, Heat, Material*)
$= E_{accumulated}$

## GENERALIZATIONS IIIB.
(The Laws)

**Work & Heat Not Equivalent, Even for Reversible Changes**

**Closed System 2nd Law**

$dS \equiv \delta Q_{rev} / T$

$T$ **is Integrating Factor for path-dependent** $\delta Q_{rev}$

**Closed System Properties**

$dU \equiv dE - dE_{kin} - dE_{pot} = TdS + dW_{rev}$
$e.g., \quad = TdS - PdV$

## GENERALIZATIONS IIIC.
(The Laws)

**Work Fully Degradable to Heat, But Not *vice versa***

***Irreversibility***

$dS_{gen} = dS - \delta Q / T \geq 0$

**Entropy "Balance"**

$S_{in}$ (*Heat, Material*)
$- S_{out}$ (*Heat, Material*) $+ S_{gen}$
$= S_{accumulated}$

## SUMMARY OF PART I.

Structure of Thermodynamics exists:
It can be learned & it should be used

Amount of material large;
Generalizations are abstract

Conceptuals confuse while simplifying
(But alternatives worse!)

Do "First Things" first,
then model & calculate

## MIXTURE IDEALITIES/REALITIES I.

| | Ideal Gas | Ideal Solution |
|---|---|---|
| Ideality | | |
| Equation of State | $PV=NRT$ | |
| Fugacity | $f_i^{ig} \equiv x_i P$ | $f_i^{is} \equiv x_i f_i^o$ |
| Reality Corrections | | |
| Multiplicative(Ratio Measure) | | |
| Equation of State | $PV = ZNRT$ | |
| Fugacity (FFFF) | $f_i \equiv x_i \phi_i P$ | $f_i \equiv x_i \gamma_i f_i^o$ |
| Additive Residual | $F \equiv F^{ig} + F^{res}$ | |
| Excess | | $F \equiv F^{is} + F^E$ |

## MIXTURE IDEALITIES/REALITIES II.

Standard States

Lewis-Randall $f_i^o = f_{Pure\ i}$ $\lim_{x_i \to 1} \gamma_i = 1$

Henry's Law $f_i^o = H_{iR}$ $\lim_{x_R \to 1} \gamma_i = 1$

Connections of *ig* and *is* corrections

*e.g.*, $f_i^o(T,P) = \phi_i^o(T,P)P$ $\gamma_i = \frac{\phi_i(T,P,x)}{\phi_i^o(T,P)}$

EOS Mixing Rules Can Yield $G^E \to \gamma_i$
Model Behavior

## SUMMARY OF PART II.

Thermodynamics Has Many Aspects
Learning/remembering math is challenge

Conceptuals Must Be Related to Measurables
Multiple complex relations

Decisions about variables required
Number of independents? = Total - Relations
Number to solve for? = Relations
Which ones? = Most convenient

## PART III:
## MULTIPLE PHASES & REACTIONS

1st & 2nd Laws for
- Properties & processes of multipart systems
- Transfer among parts, especially phases
- Equilibrium among parts, especially phases
- Reactions
  - Species
  - Independent reactions

Stability - testing if a proposed system can exist

Human representations of
- Nature's richness of phases

## DRIVING FORCES FOR CHANGE

Heat Flows from High to Low Temperature

Work Flows from High to Low "Force"
(*e.g., PV* Work from High to Low *P*)

Material Flows from Hi to Lo Chemical Potential
(Commonly, Diffuses from Hi to Lo Fugacity)

Reversible Changes/Equilibrium States
Only Differential Differences in $T, P, \mu_i$ ($S_{Gen} \equiv 0$)

Spontaneous Changes/Real Changes ($S_{Gen} > 0$)
Finite Differences in $T, P, \mu_i$ or If State Undefined
Increases with Property ($T, P, \mu_i$) Differences
Largest for Heat Flow over $T$ Difference

Biosystems Folks Usually Write Phase Transfers as Reactions

## PHASE EQUILIBRIA

**Fundamental Relations**

**Phase Equilibrium**

**Equal Chemical Potentials**

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

**Equal Fugacities**

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

**Usually, Chemical Engineers Model $f_i$**

**But Biosystems Folks Model $\mu_i$**

## REACTIONS I.

- Components & Species Composed of Atoms of Elements Bound by High Energy
  - Always Must Know the Chemical Formula
- Batch Reactor Fed Components that React to Form Species - Stoichiometry Constrains Relative Amounts of Species
  - Components for Species May Not Be Unique
  - Determine Number of "Independent" Species
- Open Reactor Fed Reactant Species Reacting to Form Product Species – Stoichiometry Fixes
- Problem Solving Requires Knowing Species
- Species May Not Be Observed (Transition State)

## REACTIONS II.

At fixed $T$, $P$, Driving Force for Reaction:

- Decrease Gibbs Energy, $g$
- Equilibrium at Minimum $g$
- Compute with ($T$, $P$, $\{\mu\}$)

$$\Delta g_R \equiv \sum \Delta g_k \equiv \sum \nu_{ik}\mu_i(T,P,\{x\}) \leq 0$$

- Combination of Energy & Entropy

$$\Delta g_R = \Delta h_k - T\Delta s_R \leq 0$$

If $\Delta g_R = 0$, No Reaction Occurs

- Living systems continue reactions (life) by insuring $\Delta g_R < 0$ using mechanisms based on energy & entropy

## STABILITY

**To Predict What Will Be Observed,**
**Use Both Differential and Global Criteria**
**No New Laws Needed**

**In General**

**Entropy Maximized Only If System is *Isolated***
**Energy Function Minimized in All Other Systems;**
**Depends on Constraint Variables –**
***e.g.,* Min *G* if *T, P* fixed while varying**
**{*x*}, phases, reaction**
***S* not maximum in ambient 2-liquid oil/water!**

## STABILITY CRITERIA

**Multiphase Systems**

**Differential Criterion - Partial Derivatives**

**Pure Fluids - Proposed Phase Unstable if**

$$\partial P / \partial v)_T > 0$$

**Mixtures - Unstable If Stability Matrix Not Positive Definite**

$$\partial \mu_i / \partial N_j)_{T,P,N_{k\neq j}}$$

**Global Criterion: Observed=Lowest Minimum**

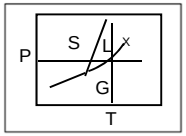
**Metastable: When Differential OK, Global Not**

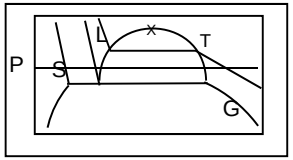
**Often Seen in Solids & Microstructured Fluids (Polymers, Biosystems, Surfactants, Colloids)**

## PHASE DIAGRAMS – NATURE'S RICHNESS

**Phase Diagrams Represent Behavior**

**Including number of independent variables**
***e.g., P/T* Plot (*F*), "vaporization"(VLE) is line,**
**On *P/v* Plot (*F*'), is region of horizontal *P, T* lines ending at volumes of saturated phases**




**Critical Points (x) Like 3-Phases, But Special**
**Some Properties (e.g., $C_p$ ) Diverge at Criticals,**
**But Do So Universally Via "Scaling Laws"**
**Multicomponent systems have great variations**

## SUMMARY OF PART III.

**Structure of Thermodynamic Fundamentals Completed**

**Connects Physics/Chemistry to Math**

**Conceptuals & Measurables for Tendencies & Finalities**

**Heat, Momentum & Mass Transport Follow Thermodynamic Driving Forces**

**Rates not Involved in Thermodynamics**

**(Transition State Thermo Used to Describe Variations of Rates)**

**Nature Has Richness in Phase Behavior**

**Representing It Is Challenging!**

## PART IV: GETTING TO THE ENGINEERING

- **Fundamentals Often Not Convenient**
  - **Must Make Specific for Problem**
  - **Desired Variable(s) May Be Embedded**
  - **Combinations of Variables May Be Adequate & Useful**
- **Solution Strategies Exposed**
- **Some Sample Results for Real Systems**

## METHODS

**Organization of Information**

**Models and Data Are Math Relations for**

**PROPERTIES (** $Z, c_P^{ig}, g^E, f_i^o$ **, . . .)** ***in terms of***

**MEASURABLES (*T, P, x, v) for Manipulation to Get***

**ALL Properties (Conceptuals of *h, s,* $f_i$*, . . .) for***

**SOLVING EQUATIONS *for Dependent Variables***

**({*x*} *,T, P, v, w, q, . . .) with***

**PARAMETERS *Depending on Molecular Makeup***

**DECISIONS *to Be Made***

***PVTx* Density, Mixing & Combining Rules (** $k_{ij}$**)**

$g^E$ **Parameterization and Standard State**

## NEW ASPECTS OF PHASE EQUILIBRIA

**All Fundamental Relations from**

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

**K-factor**

$$K_i \equiv \frac{y_i}{x_i} = \frac{\phi_i(T,v^L,\{x\})}{\phi_i(T,v^V,\{y\})} = \frac{\gamma_i\left[T,\{x\};f_i^{\,0}(T,P_i^0)\right]\exp\left[\int_{P_i^0}^{P}\frac{\bar{v}_i^L(T,\pi,\{x\})d\pi}{RT}\right]}{\phi_i^V(T,P,\{y\})P}$$

**Relative volatility**

$$\alpha_{ij} \equiv \frac{K_i}{K_j} = \frac{\varphi_j(T,v^V,\{y\})\varphi_i(T,v^L,\{x\})}{\varphi_i(T,v^V,\{y\})\varphi_j(T,v^L,\{x\})}$$

$$= \frac{\gamma_i(T,\{x\})f_i^0(T)}{\gamma_j(T,\{x\})f_j^0(T)}\frac{\varphi_j(T,P,\{y\})}{\varphi_i(T,P,\{y\})}\exp\left[\int_{P_i^0}^{P}\frac{\bar{v}_i(T,\pi,\{x\})}{RT}d\pi - \int_{P_j^0}^{P}\frac{\bar{v}_j(T,\pi,\{x\})}{RT}d\pi\right]$$

## NEW ASPECTS OF REACTIONS

**Fundamental Relations**

**Reaction Gibbs Energy Change from Fugacity**

$$\sum_i \nu_{ik}\mu_i(T,P,x) \le 0$$

$$= \sum_i \nu_{ik}\{\mu_i^o(T) + RT\ln[f_i(T,P,x)/f_i^o(T)]\}$$

**Equilibrium Constant**

$$0 = \Delta g_{Rk}^o(T) + RT\ln K_k(T)$$

**Fluids** **Liquids & Solids**

$$K_k(T) = \prod_i [x_i\phi_i(T,P,x)P]^{\nu_{ik}} = \prod_i [x_i\gamma_i(T,P,x;\ f_i^o)]^{\nu_{ik}}$$

Note: lhs is $f(T)$, but rhs appears to be $f(T, P, x)$. $f(P,x)$ cancels!

## APPLICATIONS: HOW TO DO THEM

**Carefully Express Problem**
- Are Words and Quantities Well-Defined?
- What Are the Known and Unknown Properties?
- Is the Problem Well-Posed?
- How Should "ALways Trues" Be Expressed?

**Determine Needed Accuracy, Reliability**
- Need Values to 1%, 10%, 100%?
- If in Greater Error, Will It Cause Either Physical/Chemical or Economic "Failure"?

**Structured Solution Procedure - PSALMS**

## SUMMARY OF PART IV.

**Thermodynamic Fundamentals Rearranged**
- New Quantities Defined: $K_i$, $\alpha_{ij}$, $\xi$, $\xi^{eq}$, $\gamma^+$

**Archiving Standard State Property Information** $\Delta g_f^0$, $\Delta h_f^0$, $f_i^0$

**Illustrations of How Engineers Use Fundamentals, Relations, & Data in Problem Solving**

## SUGGESTIONS FOR WORKING

- Effort *Varies* with Problem & System
- Establish *at Start* Accuracy & Generality
- Determine *Sensitivity* to Properties & Data
- Appropriate Approximations Differ for
  - Research
  - Feasibility
  - Economics
  - Equipment
  - Initialization for Iterative Solution

## PSALMS STRUCTURE / STRATEGY

**Problem -** Figure it out: write knowns, unknowns, notation, constraints, objectives as measurables

**System & boundaries –** What is it, where & what are they? Make a picture! Restate **P**roblem?

**ALways trues that are relevant –** Write general equations (*e.g.*, Laws of thermo & derived expressions), definitions; adapt to problem/system

**Model the needed quantities** – choose consistent with desired accuracy

**Solve & check -** strategize the optimal solution method, evaluate to get results, check correctness, implement, communicate, explore implications, note learning

## Problem Solving

- Structure is static
- Solving is dynamic
  - Moving through the structure
- Solving complex problems is often not linear
  - Mistakes happen from omission & commission
- Strategy to get unstuck
  - Return to **PS**
    - Really understood problem?
    - Shrewdly selected system?
  - Return to **AL**
    - Have the proper relations?
    - Are all the terms in the relations?
  - Return to **M**
    - Wrong model?
    - Too simple a model?

## SUMMARY OF STRUCTURES

**Structure helps organize knowledge & thinking**

**Structures exist for**

**Thermodynamics**
**Problem Solving**

**Use them as basis for**

**Understanding**
**Solving Problems**