THERMODYNAMICS I: BASICS

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Some Quotes about Thermodynamics I.

"A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability.

Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts."

Albert Einstein (author), Paul Arthur, Schilpp (editor). Autobiographical Notes. A Centennial Edition. Open Court Publishing Company. 1979. p. 31, quoted in Wikipedia.

Some Quotes about Thermodynamics II.

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all.

The second time you go through it, you think you understand it, except for one or two small points.

The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more."

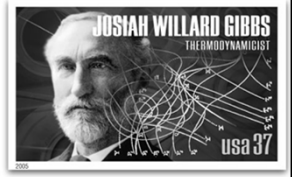
Arnold Sommerfeld, Physicist (1868-1951)

Some Quotes about Thermodynamics III.

"If your theory is found to be against the 2nd law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation."

Sir Arthur Stanley Eddington, The Nature of the Physical World (1915), quoted in Wikipedia.

"There has been nothing new in thermodynamics since J. Willard Gibbs!" Anonymous



Objectives of This Presentation

Brief overview of thermodynamic properties & relations
- "Always true" Laws & definitions
- Some always true consequences

A few applications
- Qualitative observations
  - Energy systems & chemical processing
  - Biological systems

Assumptions about audience
- Have studied ChE thermodynamics
- More interested in thermo structure than details
- Notes available, including equations & references

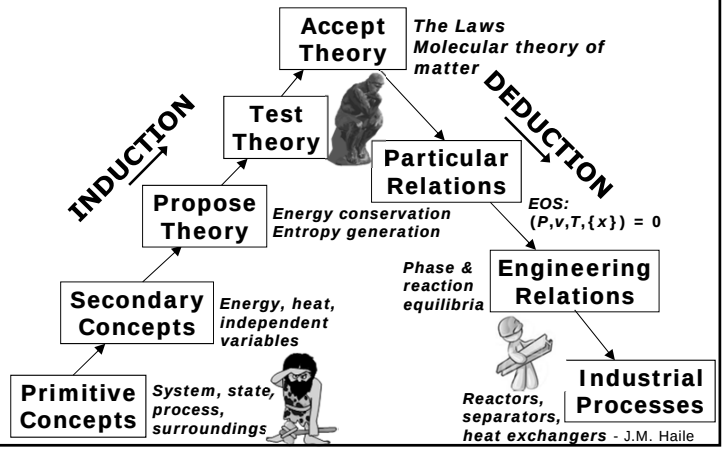
What Is Thermodynamics?

A deductive human construct to economically describe broad aspects of Nature from generalizations of behavior & mathematical rigor

Does:
- Define properties (measurables & conceptuals)
- Identify general relations among properties
  - For systems at equilibrium
  - As driving forces for transport & reaction
  - With models, used for calculating behavior
- Provide basis for evaluating feasibility, efficiency

Does not:
- Identify mechanisms
- Yield rates of transport & reaction
- Provide numerical values of properties

How Thermodynamics Evolved



What Does Thermo Teach Us? Ia.

- **1st Law:** "With mass & energy, you don't get something for nothing"

  plus "You can't throw them ***away***!"

  Open System (mass in/out at ports) steady



$(\text{Kinetic}+\text{Potential}+\text{Internal})_{in}$ - $(\text{Kinetic}+\text{Potential}+\text{Internal})_{out}$

$$\sum_{i=in} \dot{N}_i \left[e_{Ki} + e_{Pi} + h(T_i, P_i) \right] - \sum_{o=out} \dot{N}_o \left[e_{Ko} + e_{Po} + h(T_o, P_o) \right] + \dot{Q} + \dot{W}_S = 0$$

Stream Properties — Heat, Work

- Energy differences independent of process path
- Q & W_S depend on path

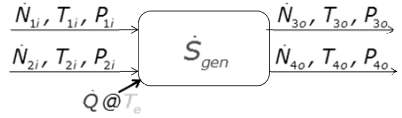
What Does Thermo Teach Us? Ib.

- **2nd Law:** "Doing what comes ***naturally*** (converting work to heat, doing mixing, combusting fuel, etc.), keeps us from breaking even"

  plus "Going against Nature costs ***work***!"

  and "The cost depends on the process"

  Open System (mass in/out at ports) steady



$$\sum_{i=in} \dot{N}s(T_i, P_i, \{x\}_i) - \sum_{o=out} \dot{N}s(T_o, P_o, \{x\}_o) + \dot{Q}/T_e + \dot{S}_{gen} = 0$$

Stream Entropies; Heat @T_e; Irreversiblities

- *Q* & S_{gen} depend on system & process

What Does Thermo Teach Us? Ic.

- Another Law:

  "Mathematics exactly describes Nature"

- Define *U, H, S, etc.* "properties" to use Math
  - Maxwell relations connect conceptuals to measurables using only PVT EoS & c_p,

$$e.g., \left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P ; \left.\frac{\partial S}{\partial T}\right|_P = \frac{C_p}{T}; \left.\frac{\partial H}{\partial P}\right|_T = \frac{V - (\partial V/\partial T)_P}{c_p}$$

  - Property differences, ΔU, ΔH, ΔS, independent of process path, unlike *Q* & *W*, so can integrate partial derivatives *conveniently*
  - But only get *differences!*

Some Consequences of the Laws Derived by Mathematics A.

- Closed System $\left(\frac{T^\alpha}{T^\beta} - 1\right)\delta Q^\beta + \left(P^\alpha - P^\beta\right)dV^\alpha \geq 0$
- Spontaneous heat/work transfer from α to β
  - Heat from high to low *T*: $\delta Q^\beta \geq 0$ if $T^\alpha > T^\beta$
  - Work from high to low *P*: $\delta W^\alpha < 0$ $(dV^\alpha > 0)$ if $P^\alpha > P^\beta$
  - Reversible only if driving forces are differential

    $T^\alpha = T^\beta + dT$; $P^\alpha = P^\beta + dP$
  - Equilibrium for no force differences & gradients

    $T^\alpha = T^\beta$; $P^\alpha = P^\beta$
- Properties of Mixtures, *F*, & Gibbs-Duhem Equation from *partial molar properties*

$$\bar{F}_i \equiv \left.\frac{\partial F}{\partial N_i}\right|_{T,P,N_{j\neq i}}; F = \sum_i N_i \bar{F}_i \neq \sum_i N_i F_{pure\,i}; \sum_i N_i d\ln \bar{F}_i - \left.\frac{\partial F}{\partial T}\right|_{P,N} dT - \left.\frac{\partial F}{\partial P}\right|_{T,N} dP = 0$$

Some Consequences of the Laws Derived by Mathematics B.

- Open system $\left(\frac{T^\alpha}{T^\beta} - 1\right)\delta Q^\beta + \left(P^\alpha - P^\beta\right)dV^\alpha + \sum_i \left[\bar{G}_i^\alpha - \left(\bar{H}_i^\beta - T\bar{S}_i^\beta\right)\right]dN_i^\alpha \geq 0$
- Diffusion from high to low $\bar{G}_i$ or f_i; $dN_i^\alpha > 0$ if $\bar{G}_i^\alpha < \bar{G}_i^\beta$ or $f_i^\alpha < f_i^\beta$
  - Equilibrium when $\bar{G}_i^\alpha = \bar{G}_i^\beta$ or $f_i^\alpha = f_i^\beta$
  - Equivalent to minimum of *G* at fixed *T* & *P*
- Reaction driving force = affinity $\mathcal{A} \equiv -\sum_i \nu_i \bar{G}_i$
  - Tendency to react when $\mathcal{A} > 0$
  - Equilibrium when $\mathcal{A} = 0$ equivalent to minimum in *G*
  - Set standard state ^{0} for each species (*T*, P^0, $\{x\}^0$, phase)
    - Tabulate standard state species formation properties $\Delta G_{if}^0(T), \Delta H_{if}^0(T)$
  - Define equilibrium constant $K(T) \equiv \exp\left[-\sum_i \nu_i \left(\Delta G_{if}^0 / RT\right)\right]$
    - Note: though terms on rhs depend on $T, P, \{x\}$, collection depends only on *T*

$$= \prod_i \left[\frac{f_i(T,P,\{x\})}{f_i^0(T)}\right]^{\nu_i}$$

- Solving problems: models give fugacities from measurables

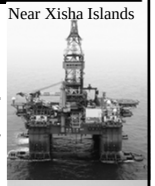
What Does Thermo Teach Us? II.

Work is needed to get more energy

Use giant structures, materials, & work to get & transport fuels, electricity, food, etc.

"You must 'invest' energy to produce energy whether it is drilling for oil or growing corn." An EROI of 5:1 is a reasonable benchmark. "Below this value, all we would have time to do is produce energy. Nothing else would be possible—no recreation, arts, or education. Those activities require that we have lots of surplus energy."

Bruce Dale, Great Lakes Bioenergy Research Center, USA


Near Xisha Islands


Hebei


3 Gorges


Mongolia

What Does Thermo Teach Us? III.

Concentration makes a difference

A barrel of sewage & a drop of wine make sewage; a barrel of wine & a drop of sewage make sewage.



The lower the concentration, the greater the molar work to purify. $W_{reversible} / N_i = -RT \ln x_i > 0$;

Huge waste treatment plants needed to extract water & remove toxics

"The solution to pollution is ***not*** dilution"

Natural concentrations of biochemicals & produced pharmaceuticals are low; even in "best case", getting extreme purity takes much useful energy


Beijing

What Does Thermo Teach Us? IV.

How to compute "best case" costs

No irreversibilities – no entropy generation

Some results:

1) not all heat can give work
2) separations require work
3) reactions have side products (usually dilute)

Even more, Nature doesn't function perfectly

"The idea of a cow is to use green stuff & water to get white stuff; but we always get some yellow stuff & brown stuff."

BASF worker, Ashville, NC



What Does Thermo Teach Us? V.

Entropy always generated in spontaneous (irreversible) action; amount "depends"

Leads to "lost work", so useful energy (or heat removal) needed to reverse such effects

Thermo also shows that extra "cost" increases with driving force ($S_{gen}\uparrow$ as property differences $\uparrow$)

Most from ΔT for heat transfer (e.g., distillation), Less via friction (ΔP), composition differences (Δx_i)

Minimize S_{gen} by

Not using heat to get work
Using heat pumps to cool
Preheating feed streams with outlet streams
...

What Does Thermo Teach Us? VI.

Component entropy may not "cause" behavior; can be from energy or other components

Demixing: Oil & water systems have lower entropy as 2 phases than as 1 phase



Ginger Dressing

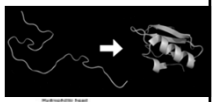
Freezing & condensing – Ice & dew have lower entropy than liquid & vapor

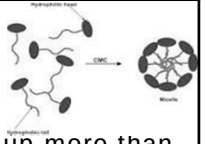


What Does Thermo Teach Us? VI.

Component entropy may not "cause" behavior; can be from energy or other components

Bio systems – Unfolded protein entropy is higher than folded





Micelles have higher entropy than separated surfactants

(Entropy of surrounding water goes up more than protein/surfactant entropy goes down)

Some Thoughts about Entropy

- Entropy as <u>"disorder"</u> is misleading
- Boltzmann view (paraphrased) "Entropy increases when the molecules can do more things." $S = k \ln W$ ⇦ # of possible states
  - Examples:
    - Volume increase gives more space, so $S\uparrow$ $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V > 0$
    - Temperature increase gives greater range of velocities, so $S\uparrow$ $\left.\frac{\partial S}{\partial T}\right|_V = \frac{C_v}{T} > 0$
    - Mixing at constant T, P gives more volume; $V\uparrow$, so $S\uparrow$
      Mix equal $N_1 = N_2 = N$ moles ig at T,P; $V = NRT / P$

$$\Delta s^{ideal\ mix}(T,P,\{x\}) = -R\sum_i x_i \ln x_i > 0$$

T,P,N_1,V ↘
T,P,N_2,V ↗
→ $T,P,2V,N_1,N_2$

    - Polymer melts/dissolves; chains can access more conformations in fluid, $S\uparrow$

What Does Thermo Teach Us? VII.

Living systems

<u>Do</u> follow Laws of Thermodynamics

Are <u>not</u> at equilibrium (equilibrium = dead!)

Are <u>open</u> to materials, energy, entropy

<u>Degrade energy</u> by(often) complex reaction schemes to convert input materials (with energy/entropy/chemical potentials) for functioning; yield outputs & heat

<u>Seek optimal conditions</u> to grow, reproduce

<u>Adapt</u> to changing conditions - <u>or die</u>

What Does Thermo Teach Us? VIII.

For common changes of state (fixed T, P), can
- **Always** know tendencies; observed changes will
- **Always** lower system gibbs energy ($\Delta G < 0$)

While thermodynamics gives tendencies
- Changes may not be observed if local paths only increase $G \Rightarrow$ *metastability* (nonequilibrium)
- Often observed in phase behavior (especially solids) & conformation (polymers & biomolecules)

Calculate conceptual properties via models
- Traditional systems directly use EoS, $c_p^{ig}(T)$, $g^E(T,x) \Rightarrow$ [activity coefficient, Δh_{mix}]
- Complex (e.g., bio) systems more challenging
  - Often involve small & uncertain differences of large & estimated positive & negative numbers

Conclusions

Thermodynamics provides much information about Nature

Not everything is possible; limits exist
- **1st Law**: For energy & mass
  - Only get something from something & away impossible
- **2nd Law**: For everything,
  - Using heat to get work yields some work & lots of heat
  - No process is perfect; always get unintended effects
  - Getting energy & overcoming degradation, mixing, etc. takes work or conversion of nutrients

Efficient technology avoids heat as energy source, minimizes S_{gen} by optimizing driving forces

Biosystems are complicated

Can get effects/requirements/tendencies of state changes from conceptual property differences related to changes in measurables using models

Some Alternative References

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