Independent Variations of TD Properties

- **Motivation**
  - Recall, a TD state is a unique (thermodynamic) description of a substance
  - identified by state variables
    - e.g., p, T, ρ, ... intensive; m, V, ... extensive)
  - How many TD properties must be known/specificed to uniquely define the **state** of a **system**?
- **Empirical evidence** (experience) suggests
  - number of ways one can **independently** vary the energy of a given substance gives the number of independent TD properties

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Reversible Work Modes

- What are independent ways to transfer energy?
  - Reversible work modes + Heat transfer
- What are reversible work modes?
  - work mode is reversible if

$$\delta W \equiv \underbrace{F}_{\text{force}}\,d\underbrace{x}_{\text{generalized displacement}}$$

    - force F is independent of direction and rate of change of process

    or

    - equivalent amount of energy transferred to system when x is increased by dx will be exactly the same amount of energy transferred from system when x is decreased by dx

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Examples of Rev. Work Modes

Mode	***dW*** (+ into system)
Fluid Compression	$-pdV$
Polarization	$\vec{E}\cdot d\left(v\vec{P}\right)$
Liquid Surface Extension	σdA

- **Simple substance**
  $\Rightarrow$ only one reversible work mode
- **Simple compressible substance**
  $\Rightarrow$ only rev. work mode is fluid compression
- Also, effect of any irreversible work modes can always be accomplished by combination of reversible work + heat transfer

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State Postulate

- Formal statement
  - "The number of independent, intensive TD properties of a *specified* substance is equal to the number of *relevant* reversible work modes (**n**) plus one."
    - *specified* substance $\Rightarrow$ must know fraction of each constituent in a mixture of substances (phases,…)
    - *relevant* modes $\Rightarrow$ only care about reversible work modes for system in question
- Does not identify which set of n+1 properties are independent
- Relationships between TD properties given by **equations of state**
  - generally for intensive TD variable, $I_{n+2} \equiv I_{n+2}(I_1, I_2, \ldots I_{n+1})$
  - e.g., $p=p(\rho,T)$

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Example: Simple Compressible Mixture

- Assume mixture of **k** pure (single-phase) substances
  - how many properties are independent?
- To *specify* substance, we need **k-1** mole fractions χ_i
  - $\chi_i \equiv n_i/n_{tot}$ where n_i is the number of moles of pure substance i (n_i is extensive, χ_i is intensive)
  - $\sum_{i=1}^{k} n_i = n_{tot};\ \sum_{i=1}^{k} \chi_i = 1$
    - so only **k**-1 mole fractions are independent

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Example (con't)

- In addition to k−1 mole fractions, state postulate says we need n+1=**2** additional independent intensive variables to define a state (n=1 for simple compressible substance)
  - $I_3 \equiv I_3(I_1, I_2, \chi_1, \ldots \chi_{k-1})$
- To determine any *extensive* property (E) of the system, we must add one additional *extensive* property (e.g., mass) to the list
  - $E_J \equiv E_J(E_1, I_1, I_2, \chi_1, \ldots \chi_{k-1})$

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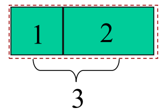
Extensive and Intensive Props.

- We can create intensive properties from extensive properties
- For example, given two systems in TD equilibrium
  $\Rightarrow\ I_J^{(1)}=I_J^{(2)}=I_J^{(3)}$
  - by additive property of extensive variables



m = mass

$$E_J^{(3)} = f(m^{(3)}, I_1, I_2) = E_J^{(1)} + E_J^{(2)}$$
$$= f(m^{(1)}, I_1, I_2) + f(m^{(2)}, I_1, I_2)$$

  - but if this is true, then we must be able to write

$$f(m, I_1, I_2) = mg(I_1, I_2)$$
$$\therefore\ E_J/m = g(I_1, I_2)$$ a (mass) **specific property**

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Specific Properties

$$\frac{E_J}{m} = g\left(I_1, I_2\right)$$

- Are intensive because they are functions ONLY of intensive properties
- Examples
  - $h \equiv H/m$ specific enthalpy
  - $v \equiv V/m$ specific volume
- Can define other types of specific props.
  - e.g., H/V volume specific enthalpy

in general, ratios of exten. props. are intensive

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