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Measurable Quantities in TD

- "Easiest" TD properties to measure: *T*, *p*, *V*, *M*
- Are there others?
  - specific "heats" (also known as heat capacities)
  - "heats" of reaction and phase change
  - compressibility coefficients
- Based on our ability to measure
  - how much heat transfer required for some change
  - change in volume/density under some fixed conditions

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Specific Heats

- Define (dn_i=0)

$$dU = \underbrace{\left.\frac{\partial U}{\partial T}\right|_V}_{\equiv C_V} dT + \left.\frac{\partial U}{\partial V}\right|_T dV \qquad dH = \underbrace{\left.\frac{\partial H}{\partial T}\right|_p}_{\equiv C_p} dT + \left.\frac{\partial H}{\partial p}\right|_T dp$$

specific heat at const. volume (C_V) **specific heat at const. pressure** (C_p)

  - extensive TD properties, also know as "frozen" specific heats if dn_i=0
- Interpretation
  - if only *pdV* work allowed $\left(dU = \delta Q - pdV\right)$

const. volume

$$dU = C_V dT$$
$$\delta Q - pdV = C_V dT$$
$$C_V = \delta Q / dT$$

const. pressure

$$dH = C_p dT$$
$$\delta Q + Vdp = C_p dT$$
$$C_p = \delta Q / dT$$

amount of energy addition as heat transfer required to change *T* of subst. by *dT*

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Specific Heats

- So historically these properties were determined from measuring temperature change for given heat addition (or equiv. work by Joule) at fixed *V* or *p*
- From Maxwell Relations, already showed

$$\left.\frac{\partial U}{\partial T}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V \Rightarrow C_V = T\left.\frac{\partial S}{\partial T}\right|_V \quad \text{similar approach} \quad C_p = T\left.\frac{\partial S}{\partial T}\right|_p$$

- Intensive versions

$$c_v = C_V/M \qquad c_p = C_p/M$$
$$\hat{c}_v = C_V\Big/\sum n_i \qquad \hat{c}_p = C_p\Big/\sum n_i$$

- Units: 1 BTU/lb_m°F = 1 cal/gC = 4.187J/gK

defined historically for H_2O at room T

air ~1 J/gK@300K

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Compressibility Coefficients

- Examine $V=V(T,p)$, with (n_i const.)

$$dV = \left.\frac{\partial V}{\partial T}\right|_p dT + \left.\frac{\partial V}{\partial p}\right|_T dp$$

Isobaric Compressibility $\quad \alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p$

Isothermal Compressibility $\quad \kappa \equiv \frac{-1}{V}\left.\frac{\partial V}{\partial p}\right|_T$

- Also

Isentropic Compressibility $\quad \beta \equiv \frac{-1}{V}\left.\frac{\partial V}{\partial p}\right|_S$

Note: many texts reverse defn. $\alpha \leftrightarrow \beta$

  - all intensive
  - for fixed composition, can write all partials in terms of: α, κ, c_p, p, v, T
  - strength materials: coeff. linear expansion = $\alpha/3$
    Young's modulus of elasticity $\propto \kappa$
  - speed of sound $\rightarrow \beta$

Compressibility Coeff: Perfect Gas

- Starting with PG state eqn.

$$V = \frac{n\bar{R}T}{p} \quad \nearrow \quad \left.\frac{\partial V}{\partial T}\right|_p = \frac{V}{T} \qquad \searrow \quad \left.\frac{\partial V}{\partial p}\right|_T = \frac{-V}{p}$$

- So

$$\alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p \qquad \kappa \equiv \frac{-1}{V}\left.\frac{\partial V}{\partial p}\right|_T$$

$$\boxed{\alpha = 1/T} \qquad \boxed{\kappa = 1/p}$$

Compressibility Coefficients

- For gen'l. simple compressible substance (dn_i=0)

$$\alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p \qquad \kappa \equiv \frac{-1}{V}\left.\frac{\partial V}{\partial p}\right|_T$$

- and $dV = \alpha V dT - \kappa V dp$

1) From reciprocity $\boxed{\left.\frac{\partial \alpha}{\partial p}\right|_T = \left.\frac{-\partial \kappa}{\partial T}\right|_p}$

2) Integrating $\boxed{\int_{V_1}^{V_2} \frac{dV}{V} = \int_{T_1}^{T_2} \alpha dT - \int_{p_1}^{p_2} \kappa dp}$

If α, κ constant

$$\ln(V_2/V_1) = \alpha \Delta T_{12} - \kappa \Delta p_{12}$$

3) From cyclic rule

$$\left.\frac{\partial p}{\partial T}\right|_V \left.\frac{\partial T}{\partial V}\right|_p \left.\frac{\partial V}{\partial p}\right|_T = -1 \qquad \boxed{\left.\frac{\partial p}{\partial T}\right|_V = \frac{\alpha}{\kappa}}$$

Specific Heats and Compress. Coeffs.

- Can develop relationship between these properties
- Start with $dS = \left.\frac{\partial S}{\partial V}\right|_T dV + \left.\frac{\partial S}{\partial T}\right|_V dT$

Showed from Maxwell Relations $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$, $\left.\frac{\partial S}{\partial T}\right|_V = \frac{1}{T}\left.\frac{\partial U}{\partial T}\right|_V$

$$\boxed{dS = \left.\frac{\partial p}{\partial T}\right|_V dV + \frac{C_V}{T} dT}$$

- With similar methods (dH)

$$\boxed{dS = \left.\frac{-\partial V}{\partial T}\right|_p dp + \frac{C_p}{T} dT}$$

- Equate

$$dp = \underbrace{\frac{C_p - C_V}{T(\partial V/\partial T)_p}}_{=(\partial p/\partial T)_V} dT - \frac{(\partial p/\partial T)_V}{(\partial V/\partial T)_p} dV$$

Specific Heats and Compress. Coeffs.

- So $\left.\frac{\partial p}{\partial T}\right|_V = \frac{C_p - C_V}{T(\partial V/\partial T)_p}$ → $C_p - C_V = \frac{\alpha}{\kappa} T \left.\frac{\partial V}{\partial T}\right|_p$
- Showed $\left.\frac{\partial p}{\partial T}\right|_V = \frac{\alpha}{\kappa}$ → $= \frac{\alpha}{\kappa} T \alpha V$

$$\boxed{C_p - C_V = T\frac{\alpha^2 V}{\kappa}}$$

- So

Perf. Gas $C_p - C_V = T\frac{(1/T)^2 V}{1/p} = \frac{pV}{T} = n\bar{R}$

1) Turns out κ>0 for all stable substances
   ⇒$C_p \geq C_V$ (or $c_p \geq c_v$)
2) For α=0 ⇒ $C_p = C_V$
3) As $T \to 0$ ⇒ $C_p \to C_V$ (exper. show κ not →0)
4) Can also show $\boxed{C_p/C_V = c_p/c_v = \kappa/\beta}$

Heats of Reaction and Phase Change

- Can examine change at specified conditions, e.g., constant T and p
  - phase change (liq)→(sol)
  - composition change A+B→C
- Energy change (increase or decrease)
  - for no work but pdV saw in 1st Law

const. volume	$Q_{12} = \Delta U_{12}$	net heat transfer (heating) required in phase change/reaction
const. pressure	$Q_{12} = \Delta H_{12}$	related to energy difference between phases or RHS vs LHS