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

Specific Heats

- Definitions

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

specific heat at const. volume

specific heat at const. pressure

  - extensive TD versions
  - typically defined for const. composition/phase (dn_i=0), then more accurately known as ***frozen specific heats***
- Interpretation (why they have these names)
  - if **only *pdV* work** allowed ($dU = \delta Q - pdV$)

const. volume $dU = C_V dT$

$$\delta Q - p\,\overset{0}{\cancel{dV}} = C_V dT$$

$$C_V = \delta Q / dT$$

const. pressure $dH = C_p dT$

$$dH = dU + d(pV) \qquad \delta Q + V\,\overset{0}{\cancel{dp}} = C_p dT$$

$$C_p = \delta Q / dT$$

amount of energy (e.g., heat transfer) required to change T of substance by dT (at const V or const p)

Specific Heats

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

$$\left.\frac{\partial U}{\partial T}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V \Rightarrow C_V = T\left.\frac{\partial S}{\partial T}\right|_V$$

similar approach⇒ $C_p = T\left.\frac{\partial S}{\partial T}\right|_p$

- Intensive versions

$$c_v = C_V/m \qquad c_p = C_p/m$$

$$\hat{c}_v = C_V/\sum n_i \qquad \hat{c}_p = C_p/\sum n_i$$

- Units (mass specific): 1 BTU/lb_m°F = 1 cal/gC = 4.187J/gK

defined historically for H_2O at room T

air ~1 J/gK@300K

Compressibility Coefficients

- Examine $V=V(T,p)$ (again typically for n_i constant)

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

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

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

- Also

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

Note: many texts reverse defn. α↔β

- α,β, κ are intensive
- For fixed composition, can write all TD 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 → function of β

Example: Ideal Gas (nonreacting)

- Starting with the Ideal Gas Law (*p*-*v*-*T* state equation) and *n*=constant

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

$$\searrow\quad \left.\frac{\partial V}{\partial p}\right|_T=\frac{-n\bar{R}T}{p^2}=\frac{-V}{p}$$

- So with

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

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

Compressibility Coefficients

- So for general simple compressible substance

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

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

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

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

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 these two dS expressions and solve for dpv

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

Specific Heats and Compress. Coeffs.

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

$$\longrightarrow C_p - C_V = \frac{\alpha}{\kappa}T\left.\frac{\partial V}{\partial T}\right|_p$$

- Also showed $\left.\frac{\partial p}{\partial T}\right|_V = \frac{\alpha}{\kappa}$

$$= \frac{\alpha}{\kappa}T\alpha V$$

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

Nonreacting Ideal Gas

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

$$\hat{c}_p - \hat{c}_v = \bar{R}$$

- So
  1) Turns out κ>0 for all stable substances
     $\Rightarrow C_p \geq C_V$ (or $c_p \geq c_v$)
  2) For $\alpha=0 \Rightarrow C_p = C_V$
  3) As $T \to 0 \Rightarrow C_p \to C_V$ (experiments 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