Entropic State Equation

- To find entropy change between 2 states of simple compressible substance without composition change, as a function of T, p

$$dS = \left.\frac{\partial S}{\partial T}\right|_p dT + \left.\frac{\partial S}{\partial p}\right|_T dp \qquad dS = C_p\, dT/T - \alpha V dp$$

$$\frac{1}{T}\left.\frac{\partial H}{\partial T}\right|_p = \frac{C_p}{T} \qquad -\left.\frac{\partial V}{\partial T}\right|_p = -\alpha V$$

- Integrating from $1 \rightarrow 2$

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{p_1}^{p_2} \alpha V dp$$

- Can follow similar procedure to show

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_v}{T} dT + \int_{V_1}^{V_2} \frac{\alpha}{\kappa} dV$$

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Enthalpic State Equation

- To find enthalpy change between 2 states of simple compressible substance without composition change, as a function of T, p
  - from H def'n. $\quad dH = dU + pdV + Vdp$
  - from Gibb's eqn. $\quad dU = TdS - pdV$
  - combine $\quad dH = TdS + Vdp$
  - but $dS{=}C_p dT/T{-}\alpha Vdp$ $\quad dH = C_p dT - \alpha VTdp + Vdp$

    $dH = C_p dT + (1 - \alpha T)\, Vdp$
- Integrating from $1 \rightarrow 2$

$$H_2 - H_1 = \int_{T_1}^{T_2} C_p dT + \int_{p_1}^{p_2} (1 - \alpha T) V dp$$

Internal Energy State Equation

- To find energy change between 2 states of simple compressible substance without composition change, as a function of T, p
  - $U=H+PV$ $\qquad dU=dH-Vdp-pdV$
  - $dH=C_p dT+Vdp-\alpha TVdp$ $\qquad dU=C_p dT-\alpha TVdp-pdV$
  - also $dV=\alpha VdT-\kappa Vdp$
    so $\qquad dU=C_p dT-\alpha TVdp-p(\alpha VdT-\kappa Vdp)$
  - then $\qquad dU=(C_p-\alpha pV)dT-(\alpha T-\kappa p)Vdp$
- Integrating from 1→2

$$U_2-U_1=\int_{T_1}^{T_2}\left(C_p-\alpha pV\right)dT-\int_{p_1}^{p_2}(\alpha T-\kappa p)Vdp$$

State Equations

- These expressions employ two integrals
  - one over T, one over p
- So is each integrand solely a function of one variable?
  - *no*
  - we can choose any path to calculate state variable change if we know initial and final states
    - e.g., constant T path then constant p path
      - need $c_p(T)$, $\alpha(T)$, $V(T)$ at fixed p (along constant p path)
      - need $\alpha(p)$, $\kappa(p)$, $V(p)$ at fixed T (along constant T path)

$$\Delta U_{12}=\int_{T_1}^{T_2}\left(C_p-\alpha pV\right)dT-\int_{p_1}^{p_2}(\alpha T-\kappa p)Vdp$$

$$\Delta H_{12}=\int_{T_1}^{T_2}C_p dT+\int_{p_1}^{p_2}(1-\alpha T)Vdp$$

$$\Delta S_{12}=\int_{T_1}^{T_2}\frac{C_p}{T}dT-\int_{p_1}^{p_2}\alpha Vdp$$