$$\Delta S_{mix} = -nR\left[x_A \ln x_A + x_B \ln x_B\right]$$

Ideal gases, const. p and T

$$A(T_1, V) = A(T_2, V)$$

heating/cooling at const. V

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_v\, dT}{T} = C_v \ln \frac{T_2}{T_1}$$

Reversible phase transitions at const. p & T

$$q_p = \Delta H_{fus}$$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} \qquad \Delta S_{trs} = \frac{\Delta H_{trs}}{T_{trs}}$$

$$H_2O(l, -10^\circ C, 1\,bar) \xrightarrow{irr} H_2O(s, -10^\circ C, 1\,bar)$$

$$\downarrow\uparrow \qquad\qquad\qquad\qquad \downarrow\uparrow$$

$$H_2O(l, 0^\circ C, 1\,bar) \rightleftharpoons H_2O(s, 0^\circ C, 1\,bar)$$

$$dU = dq^{rev} - p\, dV$$

$$dq^{rev} = T\,dS$$

$$dU = T\,dS - p\,dV$$

Rev | Irr

State variables.

$U(S, V)$ "natural variables"

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$\left(\frac{\partial U}{\partial S}\right)_V = T$

$\left(\frac{\partial U}{\partial V}\right)_S = -p$

$$dH = dU + pdV + Vdp$$

$$dH = TdS + Vdp$$

$$H(S, p)$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T \qquad \left(\frac{\partial H}{\partial p}\right)_S = V$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} C_V$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T} C_p$$

$$A(s, 0\,K) \rightleftharpoons A(s, T_m) \rightleftharpoons A(l, T_m) \rightleftharpoons A(l, T_b)$$

$$\downarrow\uparrow$$

$$A(g, T) \rightleftharpoons A(g, T_b)$$

1 bar
const. pr.

$$S(T) = S(0\,K) + \int_0^{T_m} C_{p,s} \frac{dT}{T} + \frac{\Delta H_{fus}}{T_m} + \int_{T_m}^{T_b} C_{p,l} \frac{dT}{T}$$

$$+ \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_{p,g}}{T}\, dT$$

$$dU = C_v\, dT \qquad P = \frac{RT}{V}$$

$$C_v\, dT = T\, dS - \frac{RT}{V}\, dV$$

$$dS = C_v\, d\ln T + R\, d\ln V$$

~~adiabatic~~ isolated

$$\Delta S = C_v \ln\frac{T_2}{T_1} + R \ln\frac{V_2}{V_1} \geq 0$$

$$\Delta S = \int_0^T \frac{C_{p,s}}{T}\, dT$$

$$C_p = \gamma_1 T + \gamma_2 T^3 + \cdots$$

$$dS - \frac{dq}{T} \geq 0$$ Clausius Inequality

a) heating at const V, only expansion work

$dU = dq + dw$
$= dq - P_{ext}\, dV$

$$dq_V = dU$$

$$dS - \frac{dU}{T} \geq 0$$

$$T\,dS \geq dU$$

$$dS_{V,U} \geq 0$$

$$dU_{V,S} \leq 0$$

b) heating at const. p, only expansion work

$$dq_p = dH$$

$$TdS \geq dH$$

$$dS_{p,H} \geq 0$$

$$dH_{p,S} \leq 0$$

$$dU - TdS \leq 0$$

$$dH - TdS \leq 0$$

$$G = H - TS$$

Gibb's free energy

$$A = U - TS$$

Helmholtz free energy

$$dA = dU - TdS - SdT$$

$$dG = dH - TdS - SdT$$

At const. temp

$dA = dU - TdS \leq 0$

$dG = dH - TdS \leq 0$

$dA_{T,V} \leq 0$

$dG_{P,T} \leq 0$