

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

Ideal gases, const.  $p$  and  $T$

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

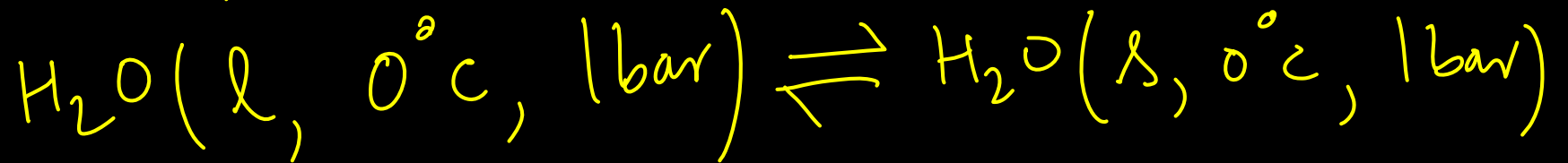
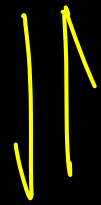
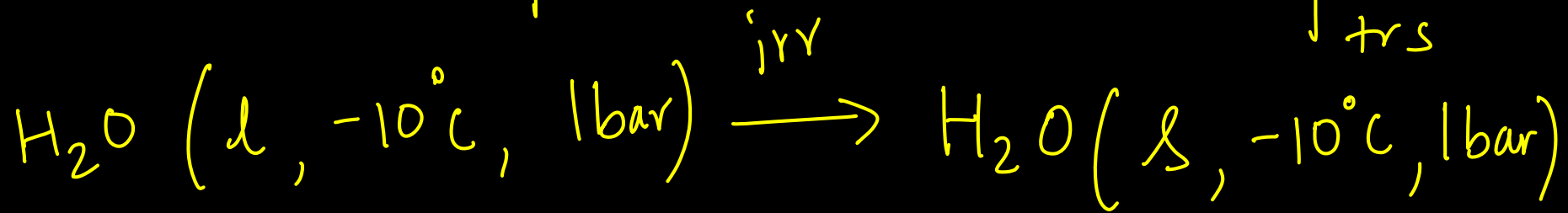
heating/cooling  
at const.  $V$

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

Reversible phase transitions at const.  $p$  &  $T$

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

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



$$dU = dq_{\text{rev}} - p dV$$

$$dq_{\text{rev}} = T dS$$

$$dU = T dS - p dV$$

Rev | Irr

State variables.

$$U(S, V)$$

"natural variables"

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

$\Downarrow T$                        $\Downarrow -P$

$$dH = dU + p dV + V dp$$

$$dH = T ds + V dp$$

$$H(S, P)$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

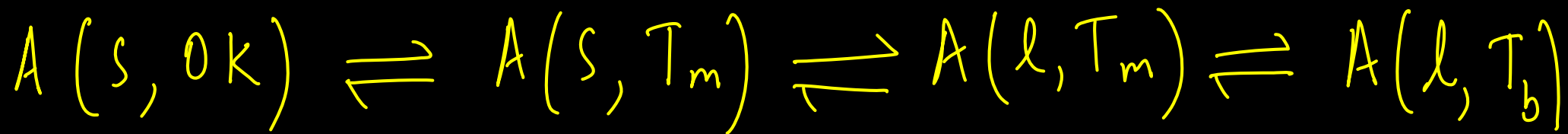
$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

$$dU = T ds - p dV$$

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

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

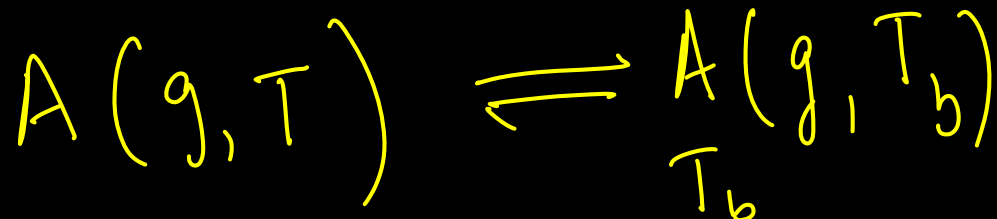
$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T} C_P$$



1 bar  
const. pr.

$$S(T) = S(0K)$$

$$+ \int_0^{T_m} \frac{C_{p,s}}{T} dT + \frac{\Delta H_{fus}}{T_m} + \int_{T_m}^{T_b} \frac{C_{p,l}}{T} dT + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^T \frac{C_{p,g}}{T} dT$$



$$dU = C_v dT$$

$$P = \frac{RT}{V}$$

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

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

~~adiabatic~~  
isolated

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

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

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

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

a) heating at const  $V$ , only expansion work

$$dU = dq + dw \\ = dq - p_{\text{ext}} dV$$

$$dq_{\text{rev}} = dU$$

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

$$TdS \geq dU$$

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

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

b) heating at const.  $p$ , only expansion work  
 $dq_p = dH$

$$TdS \geq dH$$

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

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

$$dU - TdS \leq 0$$

$A = U - TS$   
Helmholtz free energy

$$dA = dU - TdS - SdT$$

$$dH - TdS \leq 0$$

$$G = H - TS$$

Gibb's free energy

$$dG = dH - TdS - SdT$$



At const. temp

$$dA = dU - TdS \leq 0$$

$$dA_{T,V} \leq 0$$

$$dG = dH - TdS \leq 0$$

$$dG_{P,T} \leq 0$$