

$$\Delta S = C_p \ln \left\{ 1 + \left( \frac{\delta}{2T_c} \right)^2 \right\} > 0$$

$$b) T_F = T_h + \delta > T_h > T_c > T_c - \delta$$

$$\left( \frac{T_h + \delta}{T_h} \right) \left( \frac{T_c - \delta}{T_c} \right) = \left( 1 + \frac{\delta}{T_h} \right) \left( 1 - \frac{\delta}{T_c} \right)$$

$$= 1 - \left( \frac{\delta}{T_c} - \frac{\delta}{T_h} \right) - \frac{\delta^2}{T_c^2}$$

$$= 1 - \delta \left( \frac{1}{T_c} - \frac{1}{T_h} \right) - \frac{\delta^2}{T_c^2} < 1$$

$$\Delta S_B = C_p \ln \left( \frac{T_F T_c}{T_h T_c} \right) < 0$$

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## Clausius

$$dU = \delta q - P_{\text{ext}} dV$$

$$dU = \delta q_{\text{rev}} - P dV$$

$$dU = T dS - P dV$$

$$U(S, V)$$

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

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

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_T}$$

$$\delta q_{\text{rev}} - \delta q = (P - P_{\text{ext}}) dV > 0$$

$$T dS > \delta q$$

$$\boxed{dS > \frac{\delta q}{T}}$$

## CLAUSIUS

$$dS \geq \frac{dq}{T}$$

$$\Delta S \geq \int \frac{dq}{T}$$

FOR AN ISOLATED SYSTEM

$$dq = 0$$

$$\Delta S \geq 0$$

EQUALITY FOR REVERSIBLE PROCESS

$$\Delta S_U \geq 0$$

$$\Delta S_{\text{SYS}} + \Delta S_{\text{SUR}} \geq 0$$

LARGE SURR SUCH THAT  $T_{\text{SUR}} = \text{CONST}$

$$\Delta S_{\text{SUR}} = \frac{q_{\text{SUR}}}{T_{\text{SUR}}} = -\frac{q_{\text{SYS}}}{T_{\text{SUR}}}$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

$S(T, V)$

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

$$dU = C_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T} \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] dV$$

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

$$\left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right]$$

$$\left( \frac{\partial}{\partial v} \left( \frac{\partial s}{\partial T} \right)_v \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial s}{\partial v} \right)_T \right)_v$$

$$\boxed{\left( \frac{\partial}{\partial v} \frac{c_v}{T} \right)_T = \frac{1}{T} \left( \frac{\partial}{\partial v} c_v \right)_T}$$

$$= \frac{1}{T} \left( \frac{\partial}{\partial v} \left( \frac{\partial u}{\partial T} \right)_v \right)_T$$

$$\boxed{\left( \frac{\partial}{\partial T} \left( \frac{\partial s}{\partial v} \right)_T \right)_v = \left( \frac{\partial}{\partial T} \frac{1}{T} \left( p + \left( \frac{\partial u}{\partial v} \right)_T \right) \right)_v}$$

$$= - \frac{1}{T^2} \left[ p + \left( \frac{\partial u}{\partial v} \right)_T \right]$$

$$+ \frac{1}{T} \left[ \frac{\partial}{\partial T} \left( p + \left( \frac{\partial u}{\partial v} \right)_T \right) \right]_v$$

$$= - \frac{1}{T^2} \left[ p + \left( \frac{\partial u}{\partial v} \right)_T \right] + \frac{1}{T} \left( \frac{\partial p}{\partial T} \right)_v$$

$$+ \frac{1}{T} \left( \frac{\partial}{\partial T} \left( \frac{\partial u}{\partial v} \right)_T \right)_v$$

$$\frac{1}{T} \left( \frac{\partial p}{\partial T} \right)_V - \frac{1}{T^2} \left[ p + \left( \frac{\partial \bar{U}}{\partial V} \right)_T \right] = 0$$

$$\boxed{T \left( \frac{\partial p}{\partial T} \right)_V - p = \left( \frac{\partial \bar{U}}{\partial V} \right)_T} \quad !$$

THEREFORE

$$\begin{aligned} \left( \frac{\partial S}{\partial V} \right)_T &= \left( \frac{\partial p}{\partial T} \right)_V = - \left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial p} \right)_T \\ &= - \frac{\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T}{\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p} = \frac{\alpha}{\kappa} \end{aligned}$$

$$\Rightarrow \boxed{dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa} dV} \quad S(T, V)$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\alpha}{\kappa} dV$$

$S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

a)  $H = U + PV$

b)  $dH = dU + PdV + VdP$

c)  $dU = TdS - PdV$

$$dH = TdS + VdP$$

d)  $dS = \frac{1}{T}dH - \frac{V}{T}dP$

$$dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dS = \frac{C_p}{T} dT + \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right] dP$$

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

$$; \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

$$\left( \frac{\partial}{\partial p} \left( \frac{\partial s}{\partial T} \right)_p \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial s}{\partial p} \right)_T \right)_p$$

$$\left( \frac{\partial}{\partial p} \left( \frac{\partial s}{\partial T} \right)_p \right)_T = \left( \frac{\partial}{\partial p} \frac{c_p}{T} \right)_T = \frac{1}{T} \left( \frac{\partial c_p}{\partial p} \right)_T = \frac{1}{T} \left( \frac{\partial}{\partial p} \left( \frac{\partial H}{\partial T} \right)_p \right)_T$$

$$\left( \frac{\partial}{\partial T} \left( \frac{\partial s}{\partial p} \right)_T \right)_p = \left( \frac{\partial}{\partial T} \left( \frac{1}{T} \left[ \left( \frac{\partial H}{\partial p} \right)_T - v \right] \right) \right)_p$$

$$= -\frac{1}{T^2} \left[ \left( \frac{\partial H}{\partial p} \right)_T - v \right] + \frac{1}{T} \left( \frac{\partial}{\partial T} \left[ \left( \frac{\partial H}{\partial p} \right)_T - v \right] \right)_p$$

$$= -\frac{1}{T^2} \left[ \left( \frac{\partial H}{\partial p} \right)_T - v \right] - \frac{1}{T} \left( \frac{\partial v}{\partial T} \right)_p + \frac{1}{T} \left( \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial p} \right)_T \right)_p$$

$$\Rightarrow \left( \frac{\partial v}{\partial T} \right)_p = -\frac{1}{T} \left[ \left( \frac{\partial H}{\partial p} \right)_T - v \right]$$

$$\boxed{\left( \frac{\partial H}{\partial p} \right)_T = v - T \left( \frac{\partial v}{\partial T} \right)_p}$$

$$\boxed{\left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p = -v\beta}$$



$$dS = \frac{C_p}{T} dT - V\beta dp \quad S(T, p)$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{p_i}^{p_f} V\beta dp$$

$$\Delta S_{\text{SYS}} + \Delta S_{\text{SURR}} \geq 0$$

$$\Delta S_{\text{SYS}} - \frac{q_{\text{SYS}}}{T_{\text{SURR}}} \geq 0$$

$$\text{CONST } P \Rightarrow q_{\text{SYS}} = \Delta H_{\text{SYS}}$$

$$\Delta S_{\text{SYS}} - \frac{\Delta H_{\text{SYS}}}{T_{\text{SURR}}} \geq 0$$

$$\text{CONST } T \Rightarrow T_{\text{SYS}} = T_{\text{SURR}}$$

$\Delta H_{\text{SYS}} - T_{\text{SYS}} \Delta S_{\text{SYS}} \leq 0$	$(T, P)$ <u>CONST</u>
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$$\Delta G_{\text{SYS}} \leq 0$$