CARNOT CYCLE

$$\varepsilon = 1 - \frac{T_c}{T_h}$$ FOR AN IDEAL GAS.

$$\frac{q_c}{T_c} + \frac{q_h}{T_h} = 0$$ AROUND THE CYCLE

$$dS \equiv \frac{dq_{REV}}{T}$$ OPERATIONAL DEFINITION

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

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

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{C_P \mu_{JT}}{V\kappa} = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

INTERMOLECULAR FORCES

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

$$\Delta S_U \geq 0$$ = REV. PROCESSES

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

FOR SPONTANEOUS PROCESSES $\Delta S_U > 0$

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

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{c_p \mu_{JT}}{V k} = -\frac{c_p \mu_{JT}}{\left(\frac{\partial V}{\partial p}\right)_T}$$

$$= -c_p \mu_{TJ} \left(\frac{\partial p}{\partial V}\right)_T$$

$$\mu_{JT} = \frac{1}{c_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

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

$$\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T = -1$$

$$\boxed{\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T}$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$$

GIBBS and HELMHOLTZ ENERGIES

CLAUSIUS

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

$$TdS \geq dq$$

$$dU = dq + dW$$

$$dU - TdS \leq dW$$

FOR ISOTHERMAL PROCESSES

$$d(U - TS) \leq dW_{PV} + dW_{nonPV}$$

$\boxed{\text{CONSTANT VOLUME}}$ $\Rightarrow$ $dW_{PV} = -P_{ext}\,dV = 0$

$$d(U - TS) \leq dW_{nonPV} \qquad \text{CONST } (T, V)$$

$$\boxed{A \equiv U - TS}$$ HELMHOLTZ ENERGY

$$\boxed{dA \leq dW_{nonPV}}$$

$\boxed{\text{CONSTANT PRESSURE}}$ $dW_{PV} = -P_{ext}\, dV$

$$d(U - TS) + P_{ext}\, dV \leq dW_{nonPV}$$

ASSUME $P_{ext} = P$

$$d(U + PV - TS) \leq dW_{nonPV} \quad \text{CONST } (T, P)$$

$$U + PV = H$$

$$d(H - TS) \leq dW_{nonPV}$$

$\boxed{G \equiv H - TS}$ GIBBS ENERGY

$$dG \leq dW_{nonPV} \quad \text{CONST } (T, P)$$

dG = max nonPV WORK POSSIBLE

$\boxed{\text{DIFFERENTIAL FORMS}}$

$$U$$

$$H = U + PV$$

$$G = H - TS$$

$$A = U - TS$$

$$\boxed{dU = TdS - PdV} \qquad (S, V)$$

$$dH = dU + PdV + VdP = TdS + VdP \qquad (S, P)$$

$$dG = dH - TdS - SdT = -SdT + VdP \qquad (T, P)$$

$$dA = dU - TdS - SdT = -SdT - PdV \qquad (T, V)$$

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

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

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

CROSS PARTIALS $\Longrightarrow$ MAXWELL RELATIONS

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

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

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

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

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

AT CONSTANT T $\quad dG = -SdT + VdP$

$$G(T,p) - G(T,p^\circ) = \int_{p^\circ}^{p} V\,dp$$

FOR SOLIDS AND LIQUIDS

$$G(T,p) \simeq G(T,p^\circ) + V(p - p_0)$$

FOR GASES

IDEAL

$$G(T,p) \simeq G(T,p^\circ) + \int_{p^\circ}^{p} \frac{nRT}{p'}\,dp'$$

$$G(T,p) = G(T,p^\circ) + nRT\ln\left(\frac{p}{p^\circ}\right) \qquad \boxed{T\ \text{CONST}}$$

$$\left(\frac{\partial\, G/T}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{1}{T^2}G$$

$$= -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2}$$

$$= -\frac{H}{T^2}$$

$$d\left(\frac{\Delta G}{T}\right) = -\Delta H\frac{dT}{T^2} \simeq +d\left(\frac{\Delta H}{T}\right)$$

ΔH TEMP INDEPENDENT

$$\boxed{\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H(T_1)\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$