1 The First Law of Thermodynamics

$U = Q + W$
$H = U + PV$
$A = U - TS$
$G = H - TS$
$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad Q_P = \Delta H = \int C_P dT$
$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad Q_V = \Delta U = \int C_V dT$
Closed ($\Delta \equiv$ final $-$ initial) : $\Delta E_\text{p} + \Delta E_\text{k} + \Delta U = Q_\text{in} - W_\text{s, by}$
Open ($\Delta \equiv$ out $-$ in) : $\Delta E_\text{p} + \Delta E_\text{k} + \Delta H = Q_\text{in} - W_\text{s, by}$

1.1 Perfect Gases

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
$dU = C_V dT \qquad dH = C_P dT \qquad \check{C}_P - \check{C}_V = R$
Monatomic: $\check{C}_P = \frac{5}{2}R \qquad \check{C}_V = \frac{3}{2}R$
Diatomic: $\check{C}_P = \frac{7}{2}R \qquad \check{C}_V = \frac{5}{2}R$

1.2 Isothermal Process: $\{\Delta T, \Delta H, \Delta U = 0\}$

1.2.1 Reversible Expansion

$Q_{T,\text{rev,in}} = W_{T,\text{rev,by}} = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2} = -PdV$

1.2.2 Expansion Against External Pressure

$-Q_{T,\text{in}} = W_{T,\text{irrev,by}} = P_\text{ex} \Delta V$
Free expansion, $\{P_\text{ex} = 0\} : Q, W = 0$

1.3 Isobaric Process: $\{\Delta P = 0\}$

$\Delta H = Q_P = C_P \Delta T$
$W_{P,\text{by}} = P \Delta V = nR\Delta T$
$\Delta U = Q_P + W_P = C_V \Delta T$
$\Delta H = \Delta U + P \Delta V$
$\Delta T = \frac{P}{nR}(V_2 - V_1)$

1.4 Isochoric Process: $\{\Delta V = 0\}$

$W_V = 0 \qquad \Delta U = Q_V = C_V \Delta T = \frac{C_V}{nR} V (P_2 - P_1)$
$\Delta H = \Delta U + V \Delta P$

1.5 Adiabatic Reversible Process (Isentropic): $\{\Delta Q, \Delta S = 0\}$

$-dW_\text{on} = dU = -C_V dT = -PdV \qquad dH = C_P dT$
$\gamma \equiv \frac{C_P}{C_V} \qquad P_1 V_1^\gamma = P_2 V_2^\gamma \qquad T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$
$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{\check{C}_V}} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{\check{C}_P}} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma - 1}$
$W_{Q,\text{by}} = \frac{\Delta(PV)}{\gamma - 1} = \frac{nR\Delta T}{\gamma - 1}$

1.6 Reversible Polytropic Expansion

$TV^{\gamma - 1} = PV^\gamma \equiv C$
$W_{Q,\text{rev,by}} = C \int_{V_1}^{V_2} V^{-\gamma} = \frac{nR(T_2 - T_1)}{1 - \gamma} = \frac{C\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]}{1 - \gamma} = \check{C}_V (T_2 - T_1)$

1.7 Process Equipment

Nozzle / diffuser: $\Delta H = E_{k,\text{in}} - E_{k,\text{out}} \qquad W_\text{s} = 0$
Turbine / pump: $\Delta \check{H} + \Delta \check{E}_\text{k} = \pm \check{W}_\text{s,by} \qquad \check{W}_\text{s} = \int_1^2 \check{V} dP$
Heat exchanger: $\Delta \check{H} = \check{Q}_\text{in} \qquad \Delta P = 0$
Throttling device: $\Delta \check{H} = 0 \qquad \Delta P \neq 0$

1.8 Carnot Cycle (Figure 1)

$\check{W}_\text{by} : RT_\text{H} \ln \frac{\check{V}_2}{\check{V}_1} \to \check{C}_V (T_\text{H} - T_\text{C}) \to RT_\text{C} \ln \frac{\check{V}_4}{\check{V}_3} \to \check{C}_V (T_\text{C} - T_\text{H})$
$\eta = 1 + \frac{Q_\text{C}}{Q_\text{H}} = 1 - \frac{T_\text{C}}{T_\text{H}} = \frac{T_\text{H} - T_\text{C}}{T_\text{H}} = \frac{Q_\text{H} + Q_\text{C}}{Q_\text{H}} = \frac{\check{W}_\text{by}}{Q_\text{H}} \qquad \frac{Q_\text{H}}{T_\text{H}} + \frac{Q_\text{C}}{T_\text{C}} = 0$
$\check{W}_\text{by,net} = R(T_\text{H} - T_\text{C}) \ln(\check{V}_2 / \check{V}_1) \qquad$ Cooling CoP $= \frac{T_\text{C}}{T_\text{H} - T_\text{C}}$

2 The Second Law of Thermodynamics

$\Delta S_\text{univ} = \Delta S_\text{sys} + \Delta S_\text{surr}$
$dS_{T,\text{rev}} = \frac{dQ_\text{rev}}{T} \qquad \Delta S_{T,P,\text{rev}} = \frac{\Delta H}{T} \qquad \Delta S_\text{surr} = \frac{Q_\text{surr}}{T_\text{surr}}$
$\Delta S_{T,\text{sys}} = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{P_2}{P_1}$
$\Delta S_{P,\text{sys}} = C_P \ln \frac{T_2}{T_1} \qquad \Delta S_{V,\text{sys}} = C_V \ln \frac{T_2}{T_1}$
Ideal gas: $\Delta S_\text{rev,sys} = \int_{T_1}^{T_2} \frac{C_V}{T} dT + nR \ln \frac{V_2}{V_1} = \int_{T_1}^{T_2} \frac{C_P}{T} dT - nR \ln \frac{P_2}{P_1}$
Solid / liquid: $\Delta S_{P,\rho,\text{sys}} = \int_{T_1}^{T_2} \frac{C_P}{T} dT = \int_{T_1}^{T_2} \frac{C_V}{T} dT$
Phase transition: $\Delta_\text{trs} S_{T,P,\text{sys}} = \frac{\Delta_\text{trs} H}{T_\text{trs}}$
Solids in contact, adiabatic: $\Delta S_{P,V,\text{sys}} = \sum_i (n_i \check{C}_{P,i} \ln \frac{T_\text{eq}}{T_{0,i}})$
Isentropic: $n\check{C}_P \ln \frac{T_2}{T_1} = nR \ln \frac{P_2}{P_1} \qquad n\check{C}_V \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$

3 Thermodynamic Properties

3.1 Gibbs Equations

$F \in \{S, P, V, T\} : dF(t, r) = \left(\frac{\partial F}{\partial t}\right)_r + \left(\frac{\partial F}{\partial r}\right)_t$
$dU_\text{rev} = TdS - PdV \qquad T = (\partial U / \partial S)_V \qquad P = -(\partial U / \partial V)_S$
$dH_\text{rev} = TdS + VdP \qquad T = (\partial H / \partial S)_P \qquad V = (\partial H / \partial P)_S$
$dG_\text{rev} = -SdT + VdP \qquad V = (\partial G / \partial P)_T \qquad S = -(\partial G / \partial T)_P$
$dA_\text{rev} = -SdT - PdV \qquad S = -(\partial A / \partial T)_V \qquad P = -(\partial A / \partial V)_T$
$d\check{S} = \frac{\check{C}_P}{T} dT - \left(\frac{\partial \check{V}}{\partial T}\right)_P dP \qquad \left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = \frac{-\Delta H}{T^2}$

$$\Delta \check{S}(T, \check{V}) = \int_{T_1}^{T_2} \frac{\check{C}_V}{T} dT - \int_{\check{V}_1}^{\check{V}_2} \left(\frac{\partial P}{\partial T}\right)_{\check{V}} d\check{V}$$

$$\Delta \check{S}(T, P) = \int_{T_1}^{T_2} \frac{\check{C}_P}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial \check{V}}{\partial T}\right)_P dP$$

$$\Delta \check{U}(T, \check{V}) = \int_{T_1}^{T_2} \check{C}_V dT + \int_{\check{V}_1}^{\check{V}_2} \left[T \left(\frac{\partial P}{\partial T}\right)_{\check{V}} - P\right] d\check{V}$$

$$\Delta \check{U}(T, P) = \int_{T_1}^{T_2} \left[\check{C}_P - P \left(\frac{\partial \check{V}}{\partial T}\right)_P\right] dT - \int_{P_1}^{P_2} \left[T \left(\frac{\partial \check{V}}{\partial T}\right)_P + P \left(\frac{\partial \check{V}}{\partial P}\right)_T\right] dP$$

$$\Delta \check{H}(T, P) = \int_{T_1}^{T_2} \check{C}_P dT + \int_{P_1}^{P_2} \left[-T \left(\frac{\partial \check{V}}{\partial T}\right)_P + \check{V}\right] dP$$

$$\Delta \check{H}(T, \check{V}) = \int_{T_1}^{T_2} \left[\check{C}_V + \check{V} \left(\frac{\partial P}{\partial T}\right)_{\check{V}}\right] dT + \int_{\check{V}_1}^{\check{V}_2} \left[T \left(\frac{\partial P}{\partial T}\right)_{\check{V}} + \check{V} \left(\frac{\partial P}{\partial \check{V}}\right)_T\right] d\check{V}$$

$\alpha(T, P) = \frac{1}{\check{V}} \left(\frac{\partial \check{V}}{\partial T}\right)_P \qquad \kappa(T, P) = -\frac{1}{\check{V}} \left(\frac{\partial \check{V}}{\partial P}\right)_T$
$\frac{\alpha}{\kappa} = \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

3.2 Maxwell Relations

$dF = AdB + CdD \to (\partial A / \partial D)_B = (\partial C / \partial B)_D$
$U : (\partial T / \partial V)_S = -(\partial P / \partial S)_V \qquad A : (\partial P / \partial T)_V = (\partial S / \partial V)_T$
$H : (\partial T / \partial P)_S = (\partial V / \partial S)_P \qquad G : (\partial V / \partial T)_P = -(\partial S / \partial P)_T$
$\{S \to P \to V \to T \circlearrowleft\} : \left(\frac{\partial F_1}{\partial F_3}\right)_{F_2} \left(\frac{\partial F_2}{\partial F_1}\right)_{F_3} \left(\frac{\partial F_3}{\partial F_2}\right)_{F_1} = -1$

3.3 Departure Functions

$Z = Z^{(0)} + \omega Z^{(1)}$
$\check{C}_V^\text{real} = \check{C}_V^\circ + \int_{\check{V}_\infty}^{\check{V}} T \left(\frac{\partial^2 P}{\partial T^2}\right)_{\check{V}} d\check{V} \qquad \check{C}_P^\text{real} = \check{C}_P^\circ - \int_{P_0}^{P} T \left(\frac{\partial^2 \check{V}}{\partial T^2}\right)_P dP$
$\check{C}_P^\text{real} - \check{C}_V^\text{real} = T \left(\frac{\partial P}{\partial T}\right)_{\check{V}} \left(\frac{\partial \check{V}}{\partial T}\right)_P = \check{V} T \left(\frac{\alpha^2}{\kappa}\right)$
$\Delta \check{H}_{T,P}^\text{dep} = \check{H}_{T,P} - \Delta \check{H}_{T,P}^\circ$
$\Delta \check{H}_{(T_1, P_1) \to (T_2, P_2)} = \int_{T_1}^{T_2} \check{C}_P^\circ dT + \Delta \check{H}_{T_2, P_2}^\text{dep} - \Delta \check{H}_{T_1, P_1}^\text{dep}$
$\Delta \check{H}_{T,P}^\text{dep} = \left(\Delta \check{H}_{T,P}^\text{dep}\right)^{(0)} + \omega \left(\Delta \check{H}_{T,P}^\text{dep}\right)^{(1)}$
$\Delta \check{S}_{T,P}^\text{dep} = \check{S}_{T,P} - \Delta \check{S}_{T,P}^\circ$

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$$\Delta \check{S}_{(T_1,P_1)\to(T_2,P_2)} = \int_{T_1}^{T_2} \frac{\check{C}_P^\circ}{T} dT - R \ln \frac{P_2}{P_1} + \Delta \check{S}^{\text{dep}}_{T_2,P_2} - \Delta \check{S}^{\text{dep}}_{T_1,P_1}$$

$$\Delta \check{S}^{\text{dep}}_{T,P} = \left(\Delta \check{S}^{\text{dep}}_{T,P}\right)^{(0)} + \omega \left(\Delta \check{S}^{\text{dep}}_{T,P}\right)^{(1)}$$

3.4 Joule-Thomson Expansion

$\mu_{\text{JT}} = \left(\frac{\partial T}{\partial P}\right)_{\check{H}}$ $\quad \mu_{\text{JT}} {}^{>0: +\Delta V \to -\Delta T}_{<0: +\Delta V \to +\Delta T}$

4 Phase Equilibria

$$T^\alpha = T^\beta \qquad P^\alpha = P^\beta \qquad \check{G}_i^\alpha = \check{G}_i^\beta \Leftrightarrow \mu_i^\alpha = \mu_i^\beta \Leftrightarrow f_i^\alpha = f_i^\beta$$

4.1 Pure Species, 2 Phases

Clapeyron: $\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\check{H}^\beta - \check{H}^\alpha}{T(\check{V}^\beta - \check{V}^\alpha)}$

Clausius-Clapeyron (VLE): $\ln \frac{p_{\text{sat},1}}{p_{\text{sat},2}} = \frac{\Delta_{\text{vap}}\check{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ $\quad {}^{\check{V}_{(\text{g})} \gg \check{V}_{(\text{l})}}_{\Delta_{\text{vap}}\check{H} \neq f(T)}$

4.2 Non-reactive Multicomponent Multiphase Mixtures

4.2.1 Partial Molar Properties

$F \in \{H, U, G, S, V, C_P\}_{\{T,P\}}: \quad F = \sum_i n_i \bar{F}_i \quad \check{F}_i = \sum_i x_i \bar{F}_i$

$\Delta_{\text{mix}} F = F - \sum_i n_i \check{F}_i = \sum_i n_i (\bar{F}_i - \check{F}_i)$

$\Delta_{\text{mix}} \check{F} = \check{F} - \sum_i x_i \check{F}_i = \sum_i x_i (\bar{F}_i - \check{F}_i)$

$\bar{F}_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n'} \qquad F = \sum_i \bar{F}_i dn_i \qquad \bar{F}_A^\infty = \bar{F}_A(x_A \to 0)$

Gibbs-Duhem: $\sum_i n_i d\bar{F}_i = 0 \quad \sum_i x_i d\bar{F}_i = 0$

$\Delta_{\text{sln}} \check{H} = \frac{\Delta_{\text{mix}} \check{H}}{x_{\text{solute}}}$

$(\Delta_{\text{mix}} \bar{F})_i = \bar{F}_i - \check{F}_i$

$\Delta_{\text{mix}} H^\circ = 0 \qquad \Delta_{\text{mix}} V^\circ = 0$

$\Delta_{\text{mix}} S^\circ = -nR \sum_i x_i \ln x_i \qquad \Delta_{\text{mix}} G^\circ = -T \Delta_{\text{mix}} S^\circ$

4.2.2 Chemical Potential

$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} \qquad \mu_i^\star = \check{G}_i$

$\frac{\partial \mu_i}{\partial P} = \bar{V}_i \qquad \frac{\partial(\mu_i/T)}{\partial T} = \frac{-\bar{H}_i}{T^2} \qquad \frac{\partial \mu_i}{\partial T} = -\bar{S}_i$

4.3 Fugacity and Activity

$f_i^\circ = y_i P \qquad \phi_i = \frac{f_i}{y_i P} \qquad \phi_i^\star = \frac{f_i^\star}{P}$

$\gamma_i = \frac{f_{i,(\text{l})}}{x_i f_i^{\star\ominus}} \qquad a_i = x_i \gamma_i = \frac{f_{i,(\text{l})}}{f_i^{\star\ominus}}$

$\mu_i - \mu_i^{\star\ominus} = RT \ln \frac{f_i^\star}{f_i^{\star\ominus}} \qquad \mu^\beta - \mu^\alpha = RT \ln \frac{f_i^\beta}{f_i^\alpha}$

4.3.1 Vapour, Pure

$$\check{G} - \check{G}^{\star\ominus} = \int_{P_{\text{low}}}^{P} \check{V} dP = RT \ln \frac{f^\star_{(\text{v})}}{f^{\star\ominus}_{(\text{v})}}\Big|_{f^{\star\ominus}_{(\text{v})} = P_{\text{low}}}$$

$$\{\mu_i = \check{G}_i\}: \phi^\star_{(\text{v})} = \frac{f^{\star\ominus}_{(\text{v})}}{P} = e^{\frac{\Delta \check{G}^{\text{dep}}}{RT}} = e^{\frac{\Delta \check{H}^{\text{dep}} - T\Delta \check{S}^{\text{dep}}}{RT}}$$

Table: $\check{G}(T,P) = \check{H}(T,P) - T\check{S}(T,P) \qquad f^\star = P_{\text{low}} e^{\frac{\check{G} - \check{G}^{\star\ominus}}{RT}}$

EoS: $\ln \frac{f}{P_{\text{low}}} = \frac{1}{RT} \int_{P_{\text{low}}}^{P} \check{V} dP = \int_{P_{\text{low}}}^{P} \frac{Z}{P} dP$

$\qquad Z = \frac{PV}{nRT} = 1 + B'P + C'P^2 + \cdots$

$\qquad \ln \phi^\star = \ln \frac{f^\star}{P_{\text{sys}}} = B'P + \frac{C'}{2} P^2 + \cdots$

Correlation: $\ln \phi^\star = \ln \frac{f^\star_{(\text{v})}}{P} = \int_{P_{\text{low}}}^{P} \frac{Z-1}{P} dP$

$\qquad \log \phi = \log \phi^{(0)} + \omega \log \phi^{(1)}$

4.3.2 Vapour, Mixture: $\{T = T^\ominus, P = P^\ominus\}$

$$\mu_i - \mu_i^{\star\ominus} = \int_{P_{\text{low}}}^{P} \bar{V}_i dP = RT \ln \frac{f_{i,(\text{v})}}{y_i P_{\text{low}}}$$

Assume ideal, $\{\phi_{i,(\text{v})} = 1\}: f_{i,(\text{v})} = y_i P$

Lewis rule, $\{\gamma_{i,(\text{v})} = 1\}: f_{i,(\text{v})} = y_i f^\star_{i,(\text{v})}$

EoS + mixing rules: $-\int_{V_\infty}^{V} \left(\frac{\partial P}{\partial n_i}\right)_{V,T,n'} dV = RT \ln \frac{f_{i,(\text{v})}}{y_i P_{\text{low}}}$

4.3.3 Liquid, Pure: $\{T = T^\ominus, P = P^\ominus\}$

$\{P_{\text{sys}} = p_{\text{sat}}\}: f^\star_{\text{sat},(\text{l})} = f^\star_{\text{sat},(\text{v})} = \phi^\star_{\text{sat}} p_{\text{sat}}$

$\{P_{\text{sys}} > p_{\text{sat}}\}: f^\star_{(\text{l})} = f^\star_{\text{sat},(\text{l})} \mathscr{P} = \phi^\star_{\text{sat}} p_{\text{sat}} \mathscr{P}$

$\mathscr{P} \equiv \frac{f^\star_{(\text{l})}}{f^\star_{\text{sat},(\text{l})}} = e^{\left(\check{V}_{(\text{l})} \frac{P - p_{\text{sat}}}{RT}\right)}$

4.3.4 Liquid, Mixture: $\{T = T^\ominus, P = P^\ominus\}$

Lewis-Randall: $f^\circ_{i,(\text{l})} = x_i f^\star_{i,(\text{l})}$

$f_{i,(\text{l})} = \gamma_i x_i f^\star_{i,(\text{l})} = \gamma_{\mathscr{H},i} x_i \mathscr{H}_i$

$\mathscr{H}_i = \gamma_{\infty,i} f^\star_{i,(\text{l})} \qquad \gamma_{\mathscr{H},i} = \frac{\gamma_i}{\gamma_{\infty,i}}$

$\{\gamma_i \to \gamma_{\infty,i}\}: \gamma_{\mathscr{H},i} \to 1 \quad x_i \to 0$

$\frac{\partial \ln \gamma_i}{\partial P} = \frac{\bar{V}_i - \check{V}_i}{RT} \qquad \frac{\partial \ln \gamma_i}{\partial T} = \frac{\bar{H}_i - \check{H}_i}{RT^2}$

4.3.5 Excess Properties

$F \in \{H, G, S, V\}: \quad \check{F}^{\text{E}} = \check{F} - \check{F}^\circ \quad \bar{F}_i^{\text{E}} = \bar{F}_i - \bar{F}_i^\circ$

$\check{F}^{\text{E}} = \Delta_{\text{mix}} \check{F} - \Delta_{\text{mix}} \check{F}^\circ$

$\check{G}^{\text{E}} = \Delta_{\text{mix}} \check{G} - RT \sum_i x_i \ln x_i = \sum_i x_i \bar{G}_i^{\text{E}} = RT \sum_i x_i \ln \gamma_i$

$\bar{G}_i^{\text{E}} = \left(\frac{\partial [n_{\text{T}} \check{G}^{\text{E}}]}{\partial n_i}\right)_{T,P,n'} = RT \ln \gamma_i$

$\left(\frac{\partial \check{G}^{\text{E}}}{\partial P}\right)_{T,n} = \check{V}^{\text{E}} \qquad \left(\frac{\partial [\check{G}^{\text{E}}/T]}{\partial T}\right)_{P,n} = \frac{-\check{H}^{\text{E}}}{T^2} \qquad \left(\frac{\partial \check{G}^{\text{E}}}{\partial T}\right)_{P,n} = -\check{S}^{\text{E}}$

4.4 Vapour-Liquid Equilibrium: $\{T = T^\ominus, P = P^\ominus, f_{i,(\text{v})} = f_{i,(\text{l})}\}$

L-R ref., $\{x_i \to 1\}: \phi_{i,(\text{v})} y_i P = \gamma_{i,(\text{l})} x_i f_i^{\star\ominus} \qquad f_i^{\star\ominus} = \phi^\star_{\text{sat},i} p_{\text{sat}} \mathscr{P}$

Vap. & liq. ideal (Raoult's law): $\mathscr{P} = 1 \quad y_i P = x_i p_{\text{sat},i}$

Henry's law ref., $\{x_i \to 0\}: \phi_{i,(\text{v})} y_i P = \gamma_{\mathscr{H},i} x_i \mathscr{H}_i$

Ideal vapour: $y_i P = x_i \mathscr{H}_i$

Bubble point (Raoult's): $P = \sum_i x_i e^{\left(A_i - \frac{B_i}{T + C_i}\right)} \Rightarrow y_j = \frac{x_j p_{\text{sat},j}(T)}{P}$

Dew point (Raoult's): $\frac{1}{P} \sum_i \frac{y_i}{e^{\left(A_i - \frac{B_i}{T + C_i}\right)}} \Rightarrow x_j = \frac{y_j P}{p_{\text{sat},j}(T)}$

5 Figures

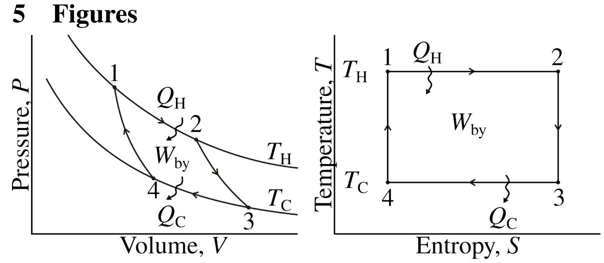

Figure 1. Carnot Cycle

References

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