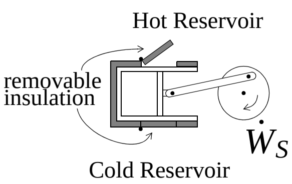
3.1 Heat Engines, Heat Pumps - The Carnot cycle



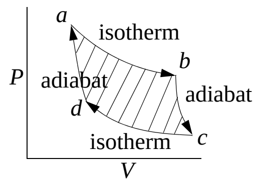
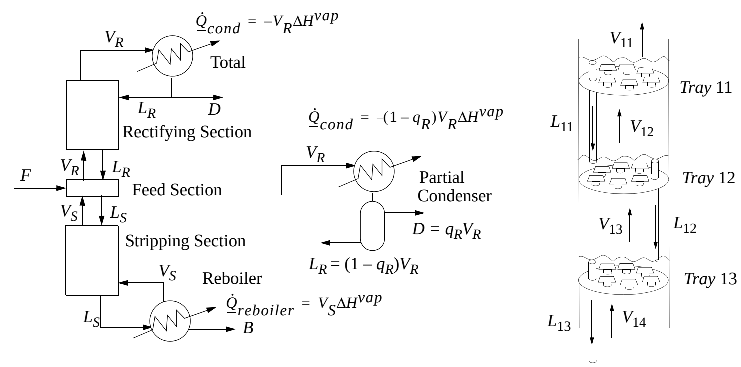


Table 3.1 Illustration of Carnot cycle calculations for an ideal gas.

Step	Type	$\underline{Q}$	$\underline{W}$
a → b	isotherm	$\underline{Q}_H = nRT_H \ln\frac{V_b}{V_a} > 0$ (ig)	$-\underline{Q}_H = -nRT_H \ln\frac{V_b}{V_a} < 0$ (ig)
b → c	adiabat	0	$\Delta U = nC_V(T_C - T_H) < 0$ (*ig)
c → d	isotherm	$\underline{Q}_C = nRT_C \ln\frac{V_d}{V_c} < 0$ (ig)	$-\underline{Q}_C = -nRT_C \ln\frac{V_d}{V_c} > 0$ (ig)
d → a	adiabat	0	$\Delta U = nC_V(T_H - T_C) > 0$ (*ig)

Carnot Heat Pump

3.2 Distillation Columns



Constant Molar Overflow

3.3 Introduction to Mixture Properties

the energy of mixing is

$$\Delta U_{mix} = U - \sum_i x_i U_i \quad 3.20$$

The enthalpy of mixing is

$$\Delta H_{mix} = H - \sum_i x_i H_i \quad 3.21$$

The volume of mixing is the volume of the mixture relative to the volumes of the components before mixing.

$$\Delta V_{mix} \equiv V - \sum_i x_i V_i \quad 3.22$$

$$U = \sum_i x_i U_i + \Delta U_{mix} \quad 3.23$$

$$H = \sum_i x_i H_i + \Delta H_{mix} \quad 3.24$$

$$V = \sum_i x_i V_i + \Delta V_{mix} \quad 3.25$$

3.4 Ideal Gas Mixtures

$$\boxed{U^{ig} = \sum_i y_i U_i^{ig}} \text{ or } \boxed{\underline{U}^{ig} = \sum_i n_i U_i^{ig}} \quad \text{(ig) } 3.26$$

$$\boxed{\underline{V}^{ig} = \left(RT\sum_i n_i\right)/P} \quad \text{(ig) } 3.27$$

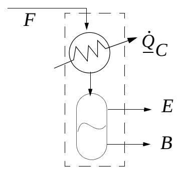
$$\boxed{\underline{H}^{ig} = \sum_i n_i U_i^{ig} + RT\sum_i n_i = \sum_i n_i\left(U_i^{ig} + RT\right) = \sum_i n_i H_i} \quad \text{(ig) } 3.28$$

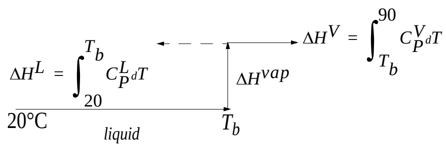
$$\boxed{H^{ig} = \sum_i y_i H_i^{ig}} \quad \text{(ig) } 3.29$$

$$\Delta U_{mix}^{ig} = 0 \qquad \Delta V_{mix}^{ig} = 0 \qquad \Delta H_{mix}^{ig} = 0 \quad 3.30$$

3.5 Ideal Solutions

Example 3.3 Condensation of mixed vapor stream





Reacting Systems

ν_i -1 - 1 1 3

ν_i is stoichiometric number

$|\nu_i|$ is stoichiometric coefficient

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2}$$

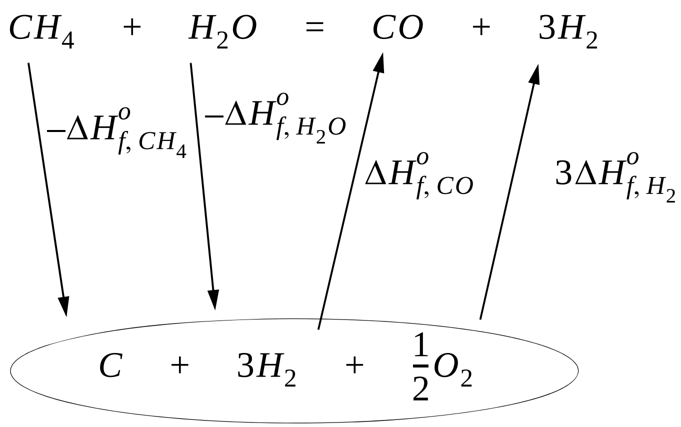
Reaction coordinate can be negative

Multiple Reactions

$$CH_3OH \leftrightarrow CO + 2H_2$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

Heat of reaction



Specified Temperature (usually 298.15K) becomes reference state,

$$\Delta H^o_R \equiv \sum \nu_i H^o_{R,\,i} \;=\; \sum \nu_i \Delta H^o_{fR,\,i} \;= \qquad 3.45$$

$$\sum_{products} |\nu_i| \Delta H^o_{fR,\,i} - \sum_{reactants} |\nu_i| \Delta H^o_{fR,\,i}$$

$\Delta H^o_T \geq 0$ Endothermic

$\Delta H^o_T \leq 0$ Exothermic

$$\Delta H^o_T \;=\; \Delta H^o_R + \int_{T_R}^{T} \Delta C_P dT$$

$$\Delta C_P \;=\; \underbrace{\sum \upsilon_i a_i} + (\sum \upsilon_i b_i)T + (\sum \upsilon_i c_i)T^2 + (\sum \upsilon_i d_i)T^3$$

$$\Delta H^o_T = \Delta H^o_R + \Delta a(T - T_R) + \frac{\Delta b}{2}(T^2 - T_R^2) + \frac{\Delta c}{3}(T^3 - T_R^3) + \frac{\Delta d}{4}(T^4 - T_R^4)$$

$$= J + \Delta a T + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3 + \frac{\Delta d}{4}T^4$$

Energy Balances - Heat of Reaction Method

$$0 \;=\; H^{in}\dot{n}^{in} - H^{out}\dot{n}^{out} + \underline{\dot{Q}} + \underline{\dot{W}}_S$$

$$H\dot{n} \;=\; \underline{\dot{H}} \;=$$

$$= \sum_{components} \dot{n}_i\left(H^o_{i,\,R} + \int_{T_R}^{T}\left(\frac{\partial H}{\partial T}\right)_{P^o,\,i} dT + \cancelto{\text{small}}{\int_{P^o}^{P}\left(\frac{\partial H}{\partial P}\right)_{T,\,i} dP}\right) + \cancelto{\text{small}}{\dot{n}\Delta H_{mix}}$$

$$\approx \sum_{components} \dot{n}_i\left(H^o_{i,\,R} + \int_{T_R}^{T} C_P dT\right)$$

$$\sum_{components} (\dot{n}_i^{in} - \dot{n}_i^{out})H^o_{i,\,R} \;=\; -\dot{\xi} \sum_{components} \nu_i H^o_{i,\,R} \;=\; -\dot{\xi}\Delta H^o_R$$

$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i} dT + \underline{\dot{Q}} + \underline{\dot{W}}_S - \dot{\xi}\Delta H_R^o \quad 3.51$$

for a given ξ, T^{in}, find

a)

b)

Energy Balances - Heat of Formation Method

$$0 = H^{in}\dot{n}^{in} - H^{out}\dot{n}^{out} + \underline{\dot{Q}} + \underline{\dot{W}}_S$$

where all enthalpies based on elements at 298.15 K

$$H^{in}\dot{n}^{in} = \sum_{components} \dot{n}_i^{in}\left(\Delta H_{fR,i}^o + \int_{T_R}^{T^{in}} C_P dT\right)$$

and

$$H^{out}\dot{n}^{out} = \sum_{components} \dot{n}_i^{out}\left(\Delta H_{fR,i}^o + \int_{T_R}^{T^{out}} C_P dT\right)$$

Better if stoichiometry not known
or many reactions.

Adiabatic Reactors (Heat of Reaction Method)

$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i} dT - \dot{\xi}\Delta H_R^o$$