

Chapters 3 Energy Balances

ENERGY BALANCES FOR COMPOSITE SYSTEMS

Carnot engine, Carnot heat pump

Work per cycle

Distillation systems

Ideal gas mixtures

Reacting systems, reaction coordinate

Heat of reaction

adiabatic processes. The Carnot engine combines them in a cycle. Consider a piston in the vicinity of both a hot reservoir and a cold reservoir as illustrated in Fig. 3.1. The insulation on the piston may be removed to transfer heat from the hot reservoir during one step of the process, and also removed from the cold side to transfer heat to the cold reservoir during another step of the process. Carnot conceived of the cycle consisting of the steps shown schematically on the P - V diagram beginning from point a . Between points a and b , the gas undergoes an isothermal expansion, absorbing heat from the hot reservoir. From point b to c , the gas undergoes an adiabatic expansion. From point c to d , the gas undergoes an isothermal compression, rejecting heat to the cold reservoir. From point d to a , the gas undergoes an adiabatic compression to return to the initial state.

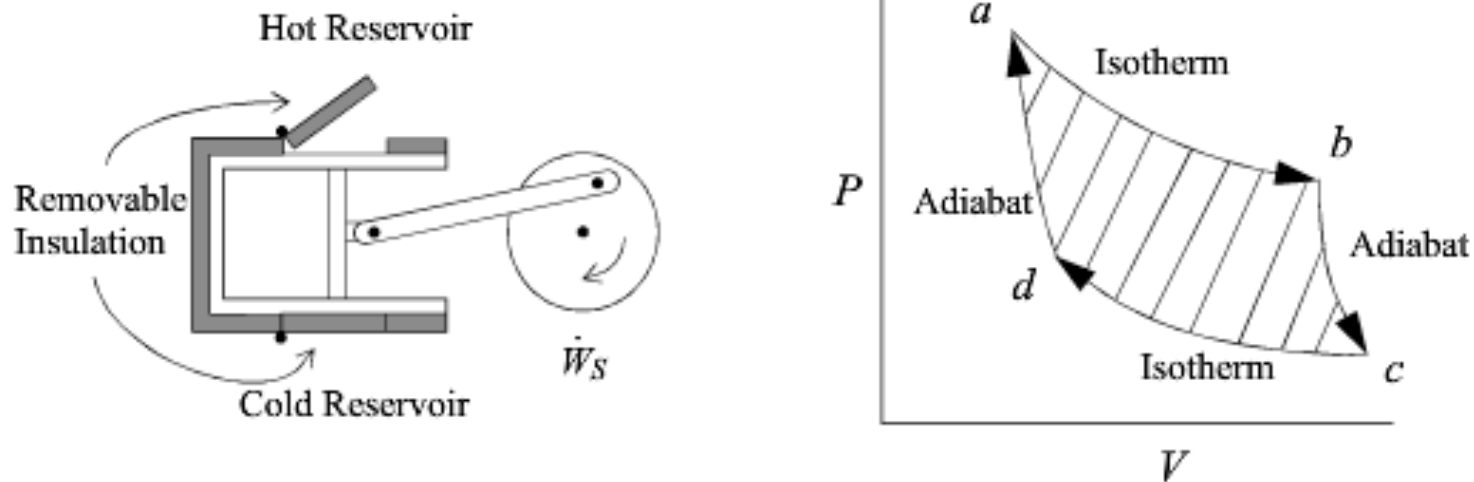


Figure 3.1 Schematic of the Carnot engine, and the Carnot P - V cycle when using a gas as the process fluid.

Macroscopic definition—Intensive entropy is a state property of the system. For a differential change in state *of a closed simple system* (no internal temperature gradients or composition gradients and no internal rigid, adiabatic, or impermeable walls),² the differential entropy change of the system is equal to the heat absorbed by the system *along a reversible path* divided by the absolute temperature of the system at the surface where heat is transferred.

$$dS \equiv \frac{dQ_{rev}}{T_{sys}}$$

4.1

where dS is the entropy change of the system. We will later show that this definition is consistent with the microscopic definition.

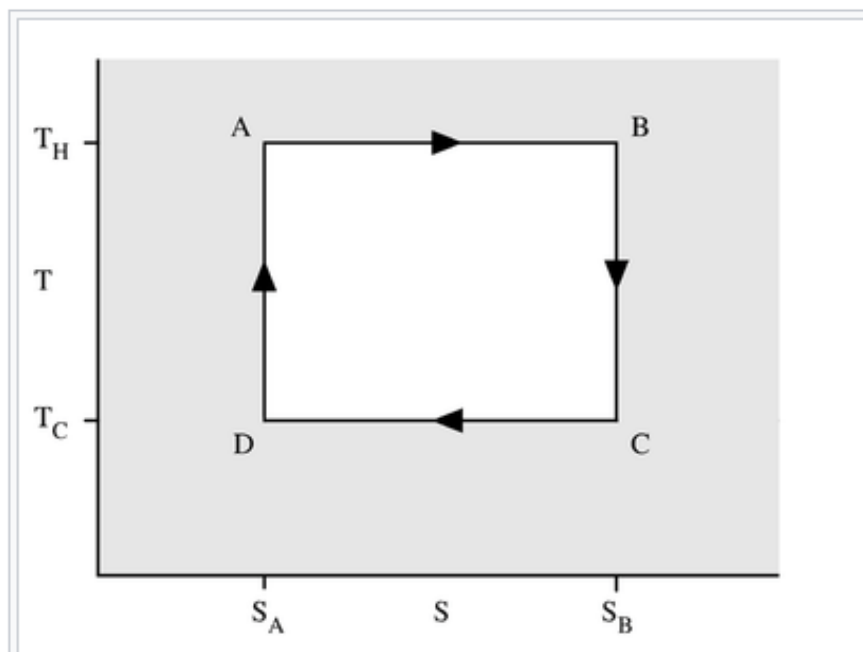
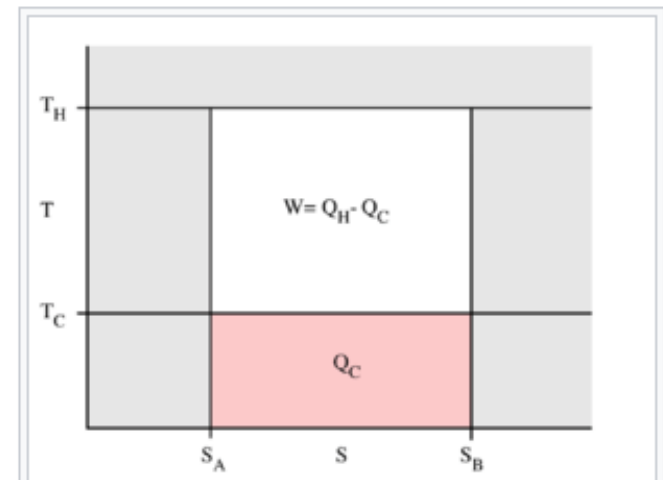


Figure 2: A Carnot cycle acting as a heat engine, illustrated on a temperature-entropy diagram. The cycle takes place between a hot reservoir at temperature T_H and a cold reservoir at temperature T_C . The vertical axis is temperature, the horizontal axis is entropy.

$$Q = \int_A^B T dS$$



A Carnot cycle taking place between a hot reservoir at temperature T_H and a cold reservoir at temperature T_C .

3.1 HEAT ENGINES AND HEAT PUMPS – THE CARNOT CYCLE

! Thermal efficiency.

thermal efficiency using the symbol η_θ :

$$\eta_\theta \equiv \frac{-\dot{W}_{S,net}}{\dot{Q}_H} \equiv \frac{\text{work output}}{\text{heat input}} \quad 3.1$$

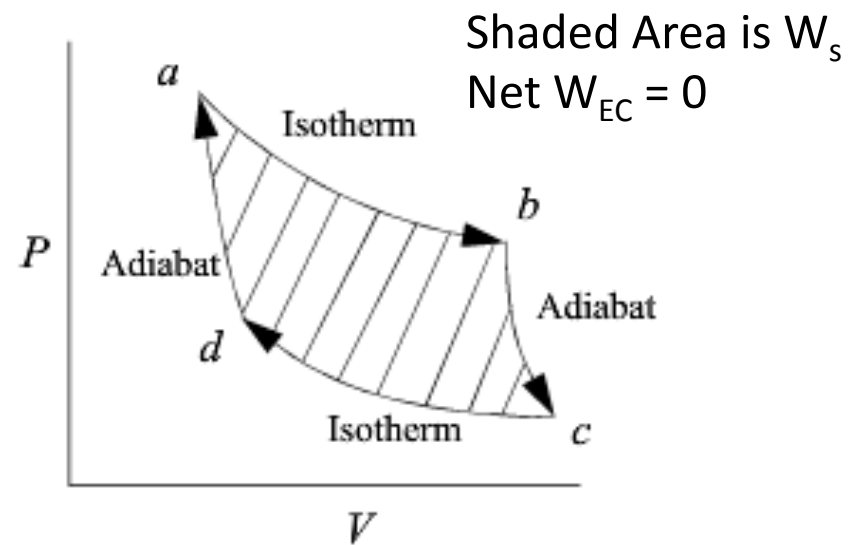
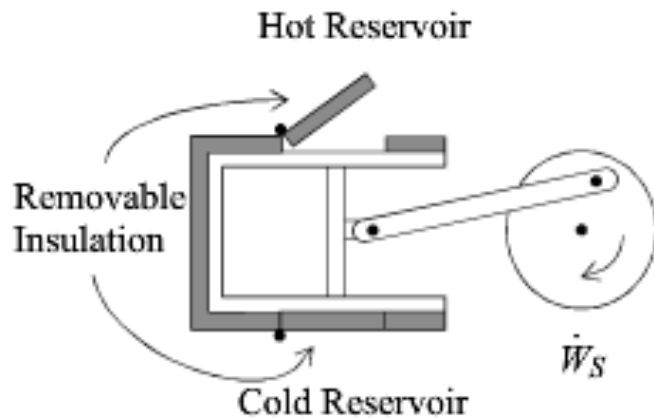


Figure 3.1 Schematic of the Carnot engine, and the Carnot P-V cycle when using a gas as the process fluid.

$$\Delta \left[m \left(U + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right) \right] = \underline{Q}_H + \underline{Q}_C + \underline{W}_{EC,net} + W_{S,net} \quad 3.2$$

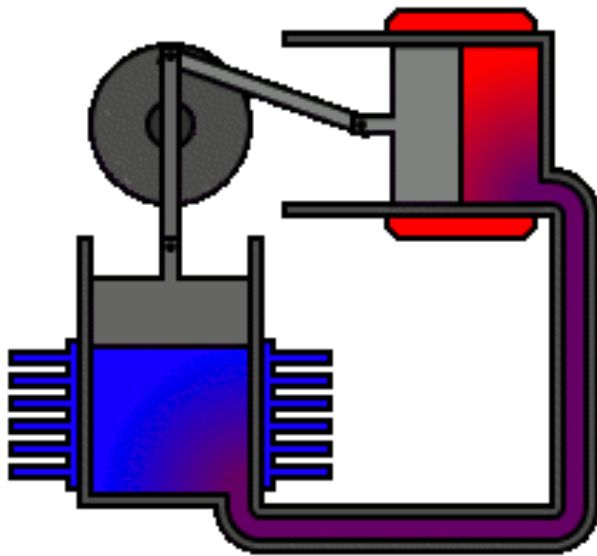
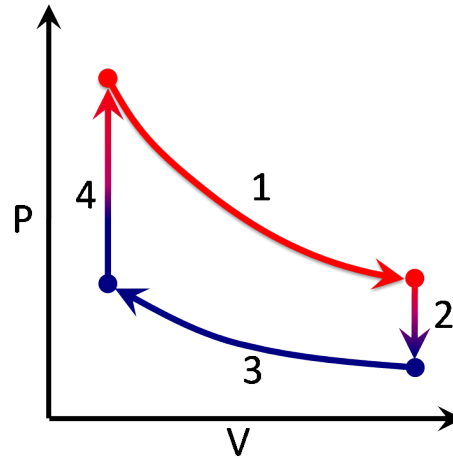
For a Cyclic Process
LHS is 0

$$-\dot{W}_{S,net} = \underline{Q}_H + \underline{Q}_C \quad 3.3$$

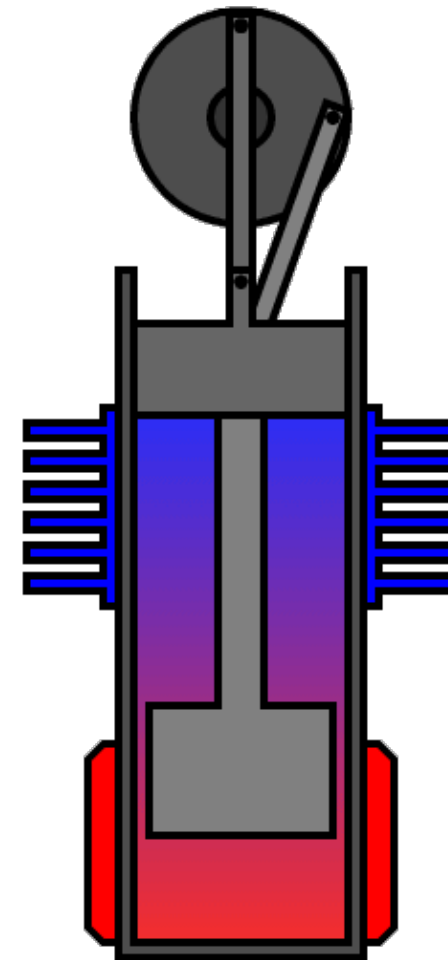
$\underline{Q}_C/\underline{Q}_H$ Negative

$$\eta_\theta = \frac{-\dot{W}_{S,net}}{\dot{Q}_H} = 1 + \frac{\underline{Q}_C}{\underline{Q}_H} \quad 3.4$$

Sterling Engine



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$$\Delta \left[m \left(U + \frac{v^2}{2g_c} + \frac{gz}{c} \right) \right] = \underline{Q}_H + \underline{Q}_C + \underline{W}_{EC,net} + \underline{W}_{S,net} \quad 3.2$$

$$-\underline{W}_{S,net} = \underline{Q}_H + \underline{Q}_C \quad 3.3$$

$$\eta_{\theta} = \frac{-\underline{W}_{S,net}}{\underline{Q}_H} = 1 + \frac{\underline{Q}_C}{\underline{Q}_H} \quad 3.4$$

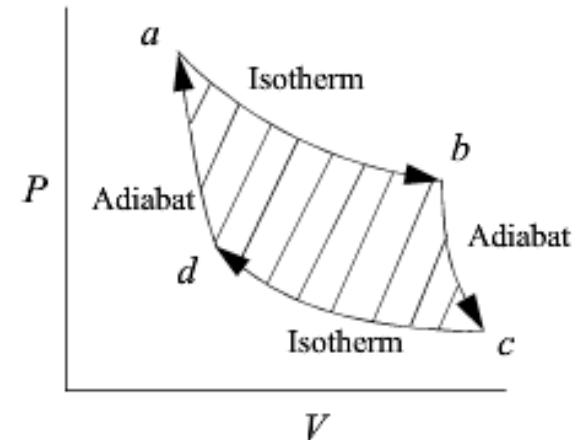
$$\frac{\underline{Q}_C}{\underline{Q}_H} = \frac{nRT_C \ln(V_d/V_c)}{nRT_H \ln(V_b/V_a)} = \frac{-T_C}{T_H} \quad 3.5$$

Table 3.1 Illustration of Carnot Cycle Calculations for an Ideal Gas.^a

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)

a. The Carnot cycle calculations are shown here for an ideal gas. There are no requirements that the working fluid is an ideal gas, but it simplifies the calculations.

Note: The temperatures T_H and T_C here refer to the hot and cold temperatures of the gas, which are not required to be equal to the temperatures of the reservoirs for the Carnot engine to be reversible. In Chapter 4 we will show that if these temperatures do equal the reservoir temperatures, the work is maximized.



Adiabatic expansion for an ideal gas

First consider the energy balance. The system will be the gas in the cylinder. The system will be closed. Since a basis is not specified, we can choose 1 mole. Since there is no mass flow, heat transfer, or shaft work, the energy balance becomes:

$$d\left[U + \cancel{\frac{v}{2g_c}} + \cancel{\frac{g}{g_c}z}\right] = \cancel{dQ} + \cancel{dW_S} + dW_{EC}$$

$$dU = -PdV$$

In this case, as we work down to step 4 in the strategy, we see that we cannot integrate the sides independently since P depends on T . Therefore, we need to combine terms before integrating.

$$C_V dT = -RT \frac{dV}{V} \quad \text{which becomes} \quad \frac{C_V}{T} dT = -\frac{R}{V} dV \quad (\text{ig}) 2.62$$

The technique that we have performed is called separation of variables. All of the temperature dependence is on the left-hand side of the equation and all of the volume dependence is on the right-hand side. Now, if we assume a constant heat capacity for simplicity, we can see that this integrates to

$$\frac{C_V}{R} \ln \frac{T}{T^i} = \ln \frac{V^i}{V} \quad (*\text{ig})$$

$$\boxed{\left(\frac{T}{T^i}\right)^{(C_V/R)} = \frac{V^i}{V}} \quad (*\text{ig}) 2.63$$

For the isothermal segments $\Delta S = Q/T$ and S is a state function so $Q_1/T_1 + Q_2/T_2 = 0$. So $Q_1/Q_2 = -T_1/T_2$.

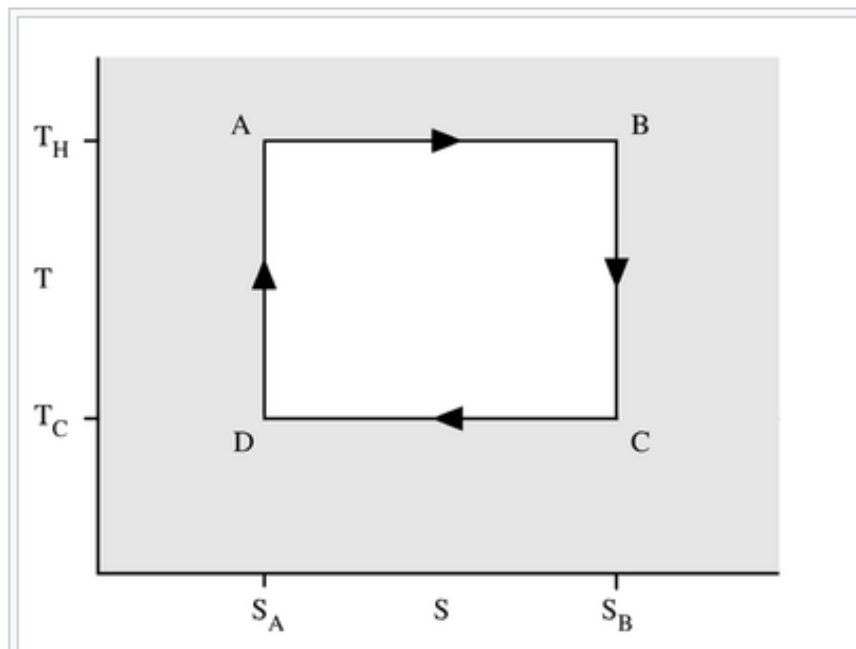


Figure 2: A Carnot cycle acting as a heat engine, illustrated on a temperature-entropy diagram. The cycle takes place between a hot reservoir at temperature T_H and a cold reservoir at temperature T_C . The vertical axis is temperature, the horizontal axis is entropy.

$$d\underline{S} \equiv \frac{dQ_{\underline{rev}}}{T_{sys}}$$

! The thermal efficiency of a heat engine is determined by the upper and lower operating temperatures of the engine.

$$\eta_{\theta} \equiv -\frac{\dot{W}_{S,net}}{\dot{Q}_H} = 1 + \frac{\dot{Q}_C}{\dot{Q}_H} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad 3.6$$

Eqn. 3.6 indicates that we cannot achieve $\eta_{\theta} = 1$ unless the temperature of the hot reservoir becomes infinite or the temperature of the cold reservoir approaches 0 K. Such reservoir temperatures are not practical for real applications. For real processes, we typically operate between the temperature of a furnace and the temperature of cooling water. For a typical power-plant cycle based on steam as the working fluid, these temperatures might be 900 K for the hot reservoir and 300 K for the cold reservoir, so the maximum thermal efficiency for the process is near 67%, theoretically. Most real power plants operate with thermal efficiencies closer to 30% to 40% owing to inherent inefficiencies in real processes.

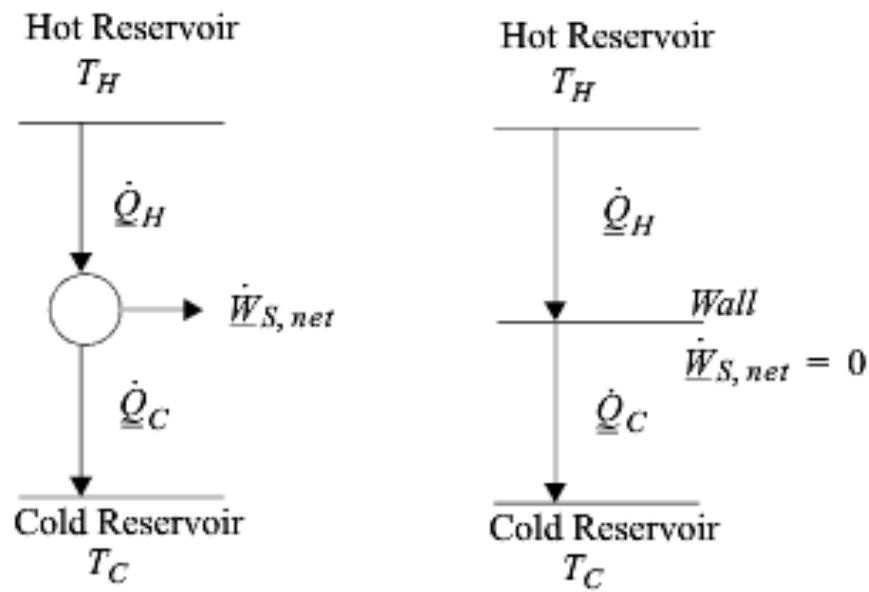


Figure 3.2 *The price of irreversibility. (a) Overall energy balance perspective for the reversible heat engine. (b) Zero work production in a temperature gradient without a heat engine, $\underline{Q}_H = \underline{Q}_C$.*

Carnot Heat Pump

For a given transfer of heat from the cold reservoir, a Carnot heat pump requires the minimum amount of work for any conceivable process. The **coefficient of performance, COP**, is the ratio of heat transferred from the cold reservoir to the work required. COP is a mirror image of thermal efficiency, reappearing in Units I and II. We want to maximize COP when the objective is to cool a refrigerator with as little work as possible.

$$COP \equiv \frac{\dot{Q}_C}{\dot{W}_{S,net}} \quad 3.7$$

$$\frac{\dot{Q}_C}{\dot{Q}_H} = \frac{nRT_C \ln(V_c/V_d)}{nRT_H \ln(V_a/V_b)} = \frac{-T_C}{T_H} \quad 3.8$$

Eqn. 3.3 still applies, and the *COP* is given by

$$\frac{\dot{W}_{S,net}}{\dot{Q}_C} = -\left(1 + \frac{\dot{Q}_H}{\dot{Q}_C}\right) = \left(\frac{T_H}{T_C} - 1\right),$$

$$COP \equiv \frac{\dot{Q}_C}{\dot{W}_{S,net}} = \left(\frac{T_H}{T_C} - 1\right)^{-1} = \frac{T_C}{T_H - T_C} \quad 3.9$$

i Coefficient of performance.

i Thermal efficiency.

$$\eta_{\theta} \equiv \frac{-\dot{W}_{S,net}}{\dot{Q}_H} \equiv \frac{\text{work output}}{\text{heat input}} \quad 3.1$$

$$\eta_{\theta} \equiv \frac{-\dot{W}_{S,net}}{\dot{Q}_H} = 1 + \frac{\dot{Q}_C}{\dot{Q}_H} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad 3.6$$

Example 3.1 Analyzing heat pumps for housing

Suppose your family is considering replacing your furnace with a heat pump. Work is necessary in order to “pump” the heat from the low outside temperature up to the inside temperature. The best you could hope for is if the heat pump acts as a reversible heat pump between a heat source (outdoors in this case) and the heat sink (indoors). The average winter temperature is 4°C, and the building is to be maintained at 21°C. The coils outside and inside for transferring heat are of such a size that the temperature difference between the fluid inside the coils and the air is 5°C. We generally refer to this as the **approach temperature**. What would be the maximum cost of electricity in (\$/kW-h) for which the heat pump would be competitive with conventional heating where a fuel is directly burned for heat. Consider the cost of fuel as \$7.00 per 10⁹J, and electricity as \$0.10 per kW-h. Consider only energy costs.

Solution: The Carnot heat pump COP, Eqn. 3.9

$$\dot{W}_{S,net} = \dot{Q}_C \left(\frac{T_H}{T_C} - 1 \right) = \dot{Q}_H \left(\frac{-T_C}{T_H} \right) \left(\frac{T_H}{T_C} - 1 \right) = \dot{Q}_H \left(\frac{T_C - T_H}{T_H} \right)$$
$$\dot{W}_{S,net} = \dot{Q}_H \frac{(-1 - 26)}{(26 + 273.15)} = -\frac{27}{299.15} \dot{Q}_H$$

where \dot{Q}_H is the heating requirement in kW. Heat pump operating cost = $(0.09) \cdot \dot{Q}_H \cdot (\theta \text{ h}) \cdot [x \text{ $/kW-h}]$, where θ is an arbitrary time and x is the cost.

Direct heating operating cost = $\dot{Q}_H \cdot (3600 \text{ s/h}) \cdot (\theta \text{ h}) \cdot (\$7/10^6 \text{ kJ})$

For the maximum cost of electricity for competitive heat pump operation, let heat pump cost = direct heating cost at the breakeven point.

$$\Rightarrow (0.09) \cdot \dot{Q}_H \cdot (\theta \text{ h}) \cdot [x \text{ $/kW-h}] = \dot{Q}_H \cdot (3600 \text{ s/h}) \cdot (\theta \text{ h}) \cdot (\$7/10^6 \text{ kJ}) \quad x = \$0.28/\text{kW-h}$$

Since the actual cost of electricity is given as \$0.10/kW-h it might be worthwhile if the heat pump is reversible and does not break down. (Purchase, installation, and maintenance costs have been assumed equal in this analysis, although the heat pump is more complex.)

3.2 DISTILLATION COLUMNS

focus is on mass and energy balances for distillation. A common model in distillation column screening is called **constant molar overflow**. In this model, the actual enthalpy of vaporization of a mixture is represented by the average enthalpy of vaporization, which can be assumed to be independent of composition for the purposes of this calculation, $\Delta H^{vap} = (\Delta H_1^{vap} + \Delta H_2^{vap})/2$. Also, all saturated liquid streams are considered to have the same enthalpy, and all saturated vapor streams are considered to have the same enthalpy. These assumptions may seem extreme, but the

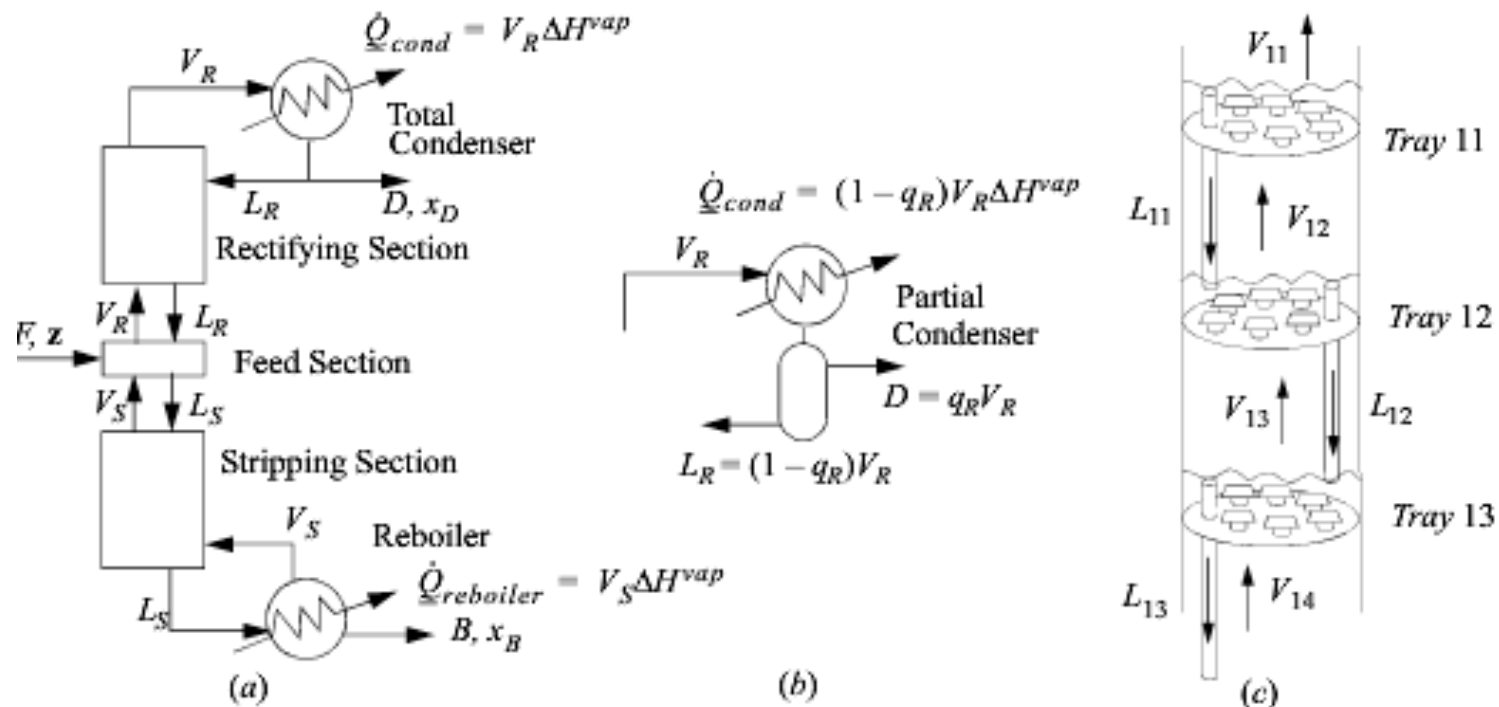


Figure 3.3 (a) Overall schematic of a distillation column with a total condenser showing five sections of a distillation column, and conventional labels; (b) a partial condenser; (c) schematic of liquid levels on bubble cap trays with the downcomers used to maintain the liquid levels.

In the constant molar overflow model for a column with one feed, the column may be represented by five sections as shown in Fig. 3.3: a feed section where the feed enters; a **rectifying** section above the feed zone; a condenser above the rectifying section which condenses the vapors and returns a portion of the liquid condensate as **reflux** L_R to ensure that liquid remains on the trays to induce the liquid-vapor partitioning that enhances the compositions.; a **stripping** section below the feed section; and a **reboiler** that creates vapors from the liquid flowing down the column.

At the bottom of the column, heat is added in the **reboiler**, causing vapor to percolate up the column until it reaches the condenser. The heat requirement in the reboiler is called the heating **duty**. B is called the **bottoms** or **bottoms product**. The ratio V_S/B is called the **boilup ratio**. The energy requirement of the reboiler is known as the reboiler **duty** and is directly proportional to the moles of vapor produced as shown in the figure.

At the top of the column, Fig. 3.3(a) shows a **total condenser** where the vapor from the top of the column is totally condensed. The liquid flow rate leaving the condenser will be $V_R = (L_R + D)$. D is called the **overhead product** or **distillate**. L_R is called the **reflux**. The proportion of reflux is characterized by the **reflux ratio**, $R = L_R/D$. A **partial condenser** may also be used as shown in (b), and the overhead product leaves as a vapor and the condensed fraction is the reflux. The cooling requirement of the condenser is called the condenser **duty** and the duty depends on whether the condenser is total or partial as shown in the figure.

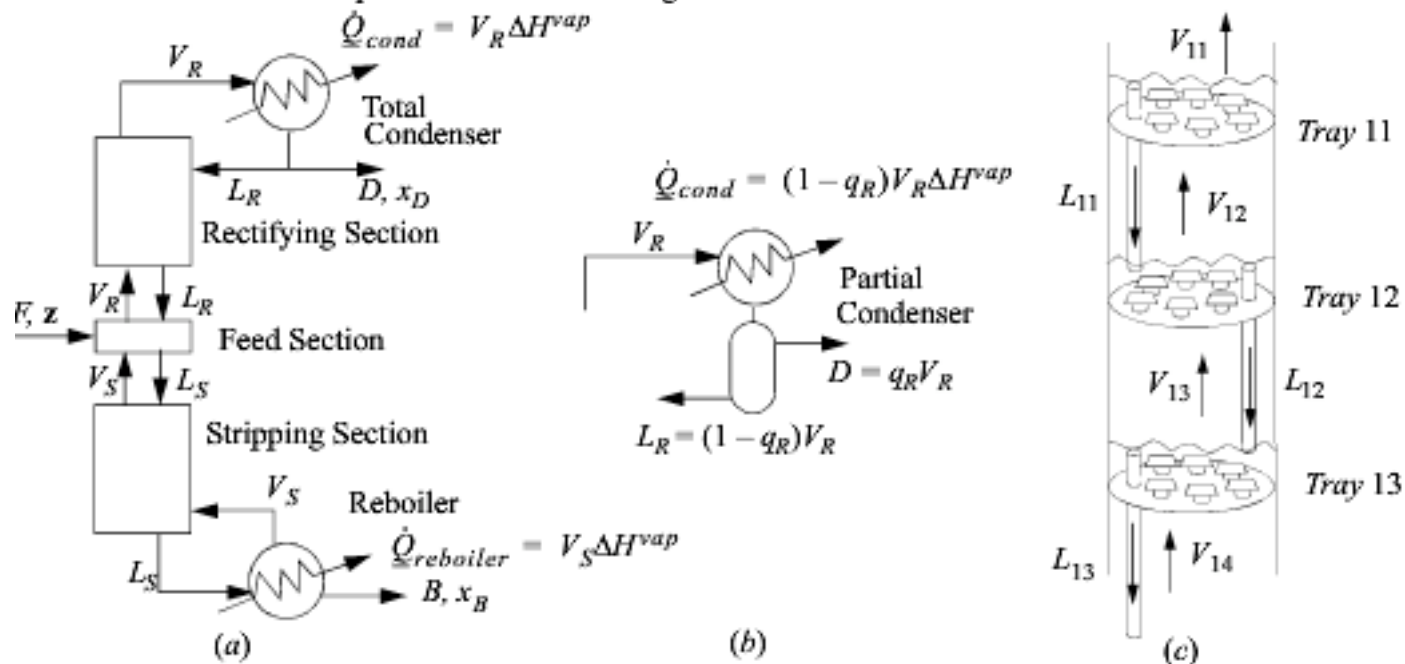


Figure 3.3 (a) Overall schematic of a distillation column with a total condenser showing five sections of a distillation column. and conventional labels; (b) a partial condenser; (c) schematic of liquid levels on bubble cap trays with the downcomers used to maintain the liquid levels.

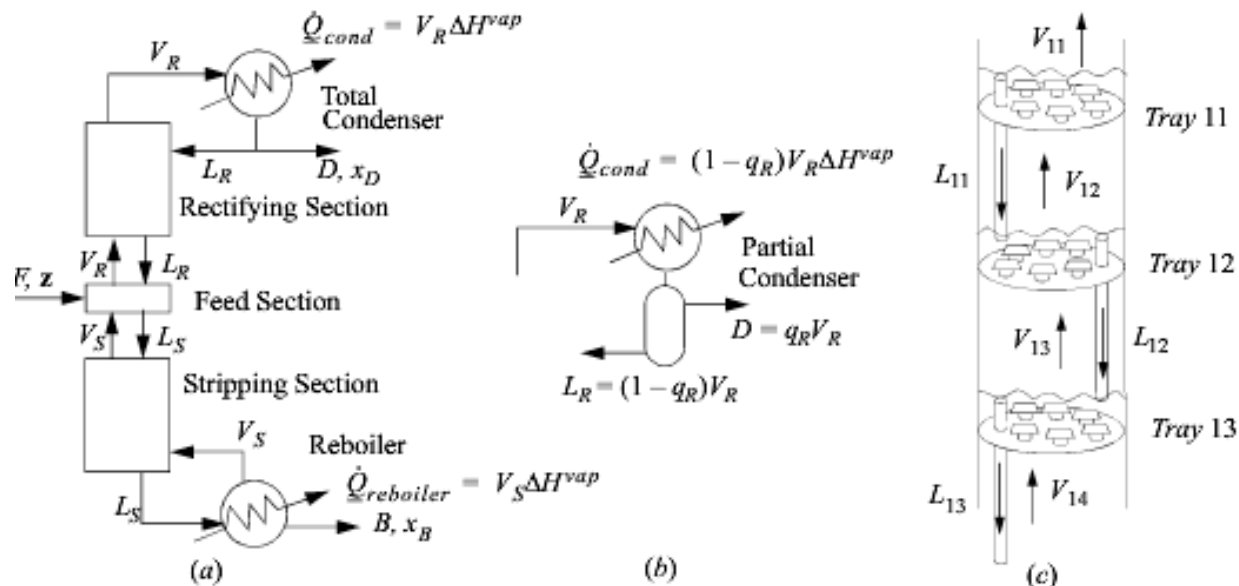


Figure 3.3 (a) Overall schematic of a distillation column with a total condenser showing five sections of a distillation column, and conventional labels; (b) a partial condenser; (c) schematic of liquid levels on bubble cap trays with the downcomers used to maintain the liquid levels.

The rectifying and stripping sections of the column have either **packing** or **trays** to provide retention of the liquid and contact with vapors. Trays are easier to introduce as shown in Fig. 3.3(c). At steady state, each tray holds liquid and the vapor flows upwards through the liquid. The trays can be constructed with holes (sieve trays) or bubble caps (bubble cap trays) or valves (valve trays). The bubble caps sketched in the figure represent a short stub of pipe with a short inverted “cup” called the “cap” with slots in the sides (slots are not shown) supported with spacing so that vapor can flow upwards through the pipe and out through the slots in the cap. A **downcomer** controls the liquid level on the tray as represented by a simple pipe extending above the surface of the tray in the figure, and in an ideal column each tray creates a separation **stage**. Using multiple stages provides greater separation. By stacking the stages, rising vapor from a lower stage boils the liquid on the next stage. At steady state, streams V_S and V_R are assumed to be saturated vapor unless otherwise noted. Streams B , L_S , and L_R are assumed to be saturated liquid unless otherwise noted. D is either assumed to be either a saturated liquid or a vapor depending on whether the condenser is total or partial, respectively. According to the **constant molar overflow** model, at steady state the vapor and liquid flow rates are constant within the stripping and rectifying sections because all the internal streams in contact are saturated, and change only at the feed section as determined by mass and energy balances around the feed section.

Example 3.2 Start-up for a distillation column

A particular bubble cap distillation column for methanol + water has 12 trays numbered from top to bottom. Each tray is composed of 4 kg of materials and holds 1 kg of liquid. The heat capacity of the tray materials is 6 J/g-K and the heat capacity of the liquid is 84 J/mol-K = 3.4 J/g-K. During start-up, the feed is turned off. Roughly 15 minutes after the reboiler is started, tray 12 has started to boil and the temperature on tray 11 begins to rise. The reboiler duty is 6 kW and the heat loss is negligible. Tray 11 starts at 25 °C and the temperature of the liquid and the tray materials is assumed the same during start-up. Assume the liquid inventory on Tray 11 is constant throughout start-up.

- (a) Tabulate and plot the temperature versus time for tray 11 until it starts to boil at 70 °C.
(b) Plot the vapor flow V_{12} as a function of time.

Solution: (a) First, recognize that $V_{11} = 0$ since tray 11 is subcooled. No liquid is flowing down to tray 11. $L_{10} = 0$ since $F = 0$ and no vapors are being condensed yet ($L_R = 0$), even though the cooling water may be flowing.

Mass balance on tray 11 (all vapors from below are being condensed during start-up, $V_{11} = 0$, $L_{10} = 0$):

$$V_{12} = L_{11} \quad 3.10$$

Mass balance on boundary around tray 11 + tray 12 ($V_{11} = 0$, $L_{10} = 0$, during start-up):

$$V_{13} = L_{12} \quad 3.11$$

State 11 is subcooled during start-up and will warm until $T_{11} = 70$:

$$H_{11} = H^L + C_p(T_{11} - T_{11}^{sat}) = H^L + C_p^L(T_{11} - 70) \quad 3.12$$

Energy balance on tray 11 during start-up (no work, no direct heat input, energy input by flow of hot vapors, negligible heat loss):

$$(m_{mat}C_p^{mat} + m_{11}C_p^L)\frac{dT_{11}}{dt} = V_{12}H^V - L_{11}H_{11} = V_{12}(\Delta H^{vap} - C_p^L(T_{11} - 70)) \quad 3.13$$

where for the last equality we have inserted Eqn. 3.10 and then Eqn. 3.12.

An energy balance on tray 12 (which is at constant temperature) gives:

$$0 = V_{13}H^V + L_{11}H_{11} - V_{12}H^V - L_{12}H^L \quad 3.14$$

Example 3.2 Start-up for a distillation column (Continued)

Using Eqn. 3.12 to eliminate H_{11} , Eqn. 3.10 to eliminate L_{11} , and Eqn. 3.11 to eliminate L_{12} ,

$$\begin{aligned} 0 &= V_{13}H^V + V_{12}H^L + V_{12}C_p^L(T_{11} - 70) - V_{12}H^V - V_{13}H^L \\ &= V_{13}\Delta H^{vap} - V_{12}\Delta H^{vap} + V_{12}C_p^L(T_{11} - 70) \end{aligned} \quad 3.15$$

$$V_{12} = \frac{V_{13}\Delta H^{vap}}{\Delta H^{vap} - C_p^L(T_{11} - 70)} \quad 3.16$$

Inserting Eqn. 3.15 into Eqn. 3.13, and recognizing the constant vapor flow rate below tray 13,

$$(m_{mat}C_p^{mat} + m_{11}C_p^L)\frac{dT_{11}}{dt} = V_{13}\Delta H^{vap} = V_S\Delta H^{vap} = \underline{Q}_{reboiler} \quad 3.17$$

where 'mat' indicates column material. Inserting values from the problem statement gives,

$$6000 \text{ J/s} = (4000 \text{ g} (6 \text{ J/g-K}) + 1000(3.4))dT_{11}/dt \Rightarrow dT_{11}/dt = 13.1 \text{ C/min} \quad 3.18$$

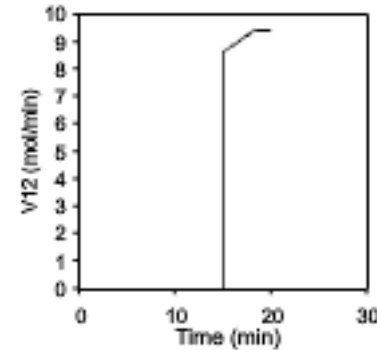
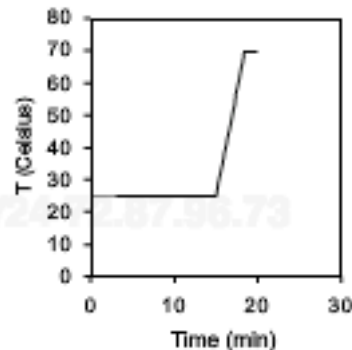
The tray will require approximately $(70 - 25)/13.1 = 3.4$ min to reach saturation temperature. The plot is shown below.

(b) The vapor flow is given by Eqn. 3.13 using $T_{11} = 25 + 13.1(t - 15)$. The average heat of vaporization is $(40.7 + 35/3)/2 = 38 \text{ kJ/mol}$. Between 15 and 18.4 min, the flow rate in mol/min

$$V_{12} = \frac{6000(60)}{38000 - 84(13.1(t - 15) - 45)} \quad 3.19$$

Note that we neglect details like imperfect mixing or bypass heating (vapor that does not get condensed) that would round the edges of the temperature profile.

t(min)	T(C)
0	25
15	25
18.4	70
20	70



3.3 INTRODUCTION TO MIXTURE PROPERTIES

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

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

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

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

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

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

3.4 IDEAL GAS MIXTURE PROPERTIES

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

The total volume of a mixture is related to the number of moles by **Amagat's law**:

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

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

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

3.5 MIXTURE PROPERTIES FOR IDEAL SOLUTIONS

The primary distinction between ideal gas mixtures and ideal solutions is the constraint of the ideal gas law for the volume of the former. Let us apply the principles of ideal solutions and ideal gas mixtures to an example that also integrates the principles of use of a reference state.

$$\boxed{U^{is} = \sum_i x_i U_i} \quad \text{or} \quad \boxed{\underline{U}^{is} = \sum_i n_i U_i} \quad 3.31$$

$$\boxed{V^{is} = \sum_i x_i V_i} \quad \text{or} \quad \boxed{\underline{V}^{is} = \sum_i n_i V_i} \quad 3.32$$

$$\boxed{H^{is} \equiv U^{is} + PV^{is} = \sum_i x_i (U_i + PV_i) = \sum_i x_i H_i} \quad \boxed{\underline{H}^{is} = \sum_i n_i H_i} \quad 3.33$$

$$\boxed{\Delta U_{mix}^{is} = 0 \quad \Delta V_{mix}^{is} = 0 \quad \Delta H_{mix}^{is} = 0} \quad 3.34$$

Example 3.3 Condensation of a vapor stream

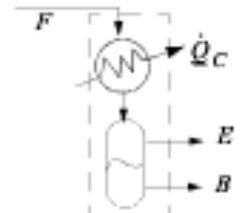
A vapor stream of wt fractions 45% H₂O, 40% benzene, 15% acetone flows at 90°C and 1 bar into a condenser at 100 kg/h. The stream is condensed and forms two liquid phases. The water and benzene can be considered to be totally immiscible in one another. The acetone partitions between the benzene and water layer, such that the *K*-ratio, $K = (\text{wt. fraction in the benzene layer})/(\text{wt. fraction in the water layer}) = 0.9$.³ The liquid streams exit at 20°C and 1 bar. Determine the cooling duty, \dot{Q}_C for the condenser. Assume the feed is an ideal gas and the liquid streams are ideal solutions once the immiscible component has been eliminated.

Solution: A schematic of the process is shown below. Using \dot{m}_1 as the flow rate of acetone in *E* and \dot{m}_2 as the flow rate in stream *B*, the *K*-ratio constraint is

$$\dot{m}_1/(\dot{m}_1 + 40) = 0.9(\dot{m}_2/(\dot{m}_2 + 45)) = 0.9((15 - \dot{m}_1)/(15 - \dot{m}_1 + 45))$$

where the acetone mass balance has been inserted in the second equality.

Using the first and third arguments, a quadratic equation results, which leads to $\dot{m}_1 = 6.6$ kg/h, and $\dot{m}_2 = 15 - 6.6 = 8.4$ kg/h.



Basis: 100 kg/h Feed			
kg/h	F	E	B
H ₂ O	45	—	45
Benzene	40	40	—
Acetone	15	6.6	8.4

Converted to kmol/h			
kmol/h	F	E	B
H ₂ O	2.5	—	2.5
Benzene	0.5	0.5	—
Acetone	0.26	0.11	0.15

The energy balance for the process side of the dotted boundary is:

$$0 = \dot{n}_F H_F - \dot{n}_E H_E - \dot{n}_B H_B + \dot{Q}_C \quad 3.35$$

We are free to choose a reference state for each component. Note that if the reference state is chosen as liquid at 20°C, then the enthalpies of *E* and *B* will both be zero since they are at the reference state temperature and pressure and the enthalpy of mixing is zero for the ideal solution assumption. This choice will greatly reduce the number of calculations. The energy balance with this reference state simplifies to the following:

$$\dot{n}_F H_F = -\dot{Q}_C \quad 3.36$$

The enthalpy of *F* as an ideal gas is given by Eqn. 3.28:

$$\dot{n}_F H_F = \sum_i \dot{n}_i H_i = \dot{n}_{F, H_2O} H_{F, H_2O} + \dot{n}_{F, benz} H_{F, benz} + \dot{n}_{F, acet} H_{F, acet} \quad 3.37$$

Refer back to Fig. 2.6 on page 65 to review the paths for calculation relative to a reference state. The path used here is similar to Fig. 2.6(a). To calculate the enthalpy for components in F , we can construct a path between the reference state and the feed state going through the normal boiling point, T_b , where the heat of vaporization is known.

$$\Delta H^L = \int_{20}^{T_b} C_p^L \delta T \quad \xrightarrow{\Delta H^{vap}} \quad \Delta H^V = \int_{T_b}^{80} C_p^V \delta T$$

20°C
liquid
 T_b

The enthalpy of a component in the feed stream is a sum of the three steps, $H_{i,F} = \Delta H^L + \Delta H^{vap} + \Delta H^V$. Note that $T_b > 90^\circ\text{C}$ for water. The ΔH^V term is calculated with the same formula, but results in a negative contribution as shown by the dotted line in the path calculation schematic. For benzene and acetone, $T_b < 90^\circ\text{C}$, so the path shown by the solid line is used for ΔH^V . Note that, although the system is below the normal boiling point of water at 1 bar, the water can exist as a component in a mixture.

Using the heat capacity polynomials, and tabulating the three steps shown in the pathway schematic, programming the enthalpy integrals into Excel or MATLAB provides

$$\begin{aligned} H_{F,H_2O} &= 6058 + 40656 - 342 = 46372 \text{ J/mol} \\ H_{F,benz} &= 8624 + 30765 + 994 = 40383 \text{ J/mol} \\ H_{F,acet} &= 4639 + 30200 + 2799 = 37638 \text{ J/mol} \end{aligned}$$

Note that the last term in the sum is negative for water because the feed temperature of the mixture is below the normal boiling temperature. The cooling duty for the condenser is

$$\dot{Q}_C = -(2.5(46372) + 0.5(40383) + 0.26(37638)) = -146 \text{ kJ/h}$$

3.6 ENERGY BALANCE FOR REACTING SYSTEMS

$$v_1 C_1 + v_2 C_2 + v_3 C_3 + v_4 C_4 = 0$$

$$d\xi = dn_i / v_i \quad 3.39$$

$$\boxed{n_i^f = n_i^i + v_i \xi} \quad 3.40$$

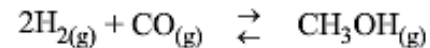
$$\boxed{\dot{n}_i^{out} = \dot{n}_i^{in} + v_i \dot{\xi}} \quad 3.41$$

$$\boxed{\dot{n}^{out} = \dot{n}^{in} + \dot{\xi} \sum_i v_i} \quad 3.42$$

1. The reaction coordinate is in some texts called the **extent of reaction**. This is misleading because depending on conditions, it can be less than one at complete conversion, or it can be negative.
2. Another common measure of reaction progress is **conversion**. In reaction engineering, it is common to follow the conversion of a particular reactant species, say, species A . If X_A is the conversion of A , then $n_A = n_A^{in}(1 - X_A)$, and $X_A = a \xi / n_A^{in}$, where a is the stoichiometric coefficient for A as written in the reaction.

Example 3.4 Stoichiometry and the reaction coordinate

Five moles of hydrogen, two moles of CO, and 1.5 moles of CH₃OH vapor are combined in a closed system methanol synthesis reactor at 500 K and 1 MPa. Develop expressions for the mole fractions of the species in terms of the reaction coordinate. The components are known to react with the following stoichiometry:



Solution: Although the reaction is written as though it will proceed from left to right, the direction of the actual reaction does not need to be known. If the reverse reaction occurs, this will be obvious in the solution because a negative value of ξ will be found. The task at hand is to develop the mole balances that would be used toward determining the value of ξ . The table below presents a convenient format.

	n^i	n^f
H ₂	5	$5 - 2\xi$
CO	2	$2 - \xi$
CH ₃ OH	1.5	$1.5 + \xi$
n_T		$8.5 - 2\xi$

The total number of moles at any time is $8.5 - 2\xi$. The mole fractions are

$$y_{\text{H}_2} = \frac{n_{\text{H}_2}^f}{n_T} = \frac{5 - 2\xi}{8.5 - 2\xi}$$

$$y_{\text{CO}} = \frac{2 - \xi}{8.5 - 2\xi}$$

$$y_{\text{CH}_3\text{OH}} = \frac{1.5 + \xi}{8.5 - 2\xi}$$

To ensure that all $n_i^f \geq 0$, the acceptable upper limit of ξ is determined by CO, and the acceptable lower limit is determined by CH₃OH,

$$-1.5 \leq \xi \leq 2$$

Standard State Heat of Reaction

effects. Because enthalpies are state properties, we can use **Hess's law** to calculate the enthalpy change. Hess's law states that the enthalpy change of a reaction can be calculated by summing any component reactions, or by calculating the reaction enthalpy along a convenient reaction pathway

ments is known as the **standard heat (or enthalpy) of formation**. The enthalpy change for "decomposing" the reactants is the negative of the heat of formation.

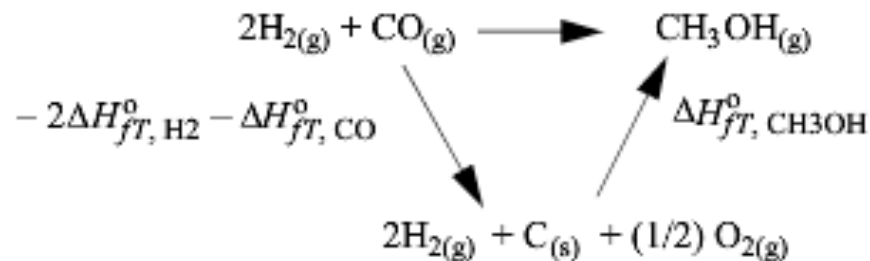


Figure 3.4 Illustration of the calculation of the standard heat of reaction by use of standard heats of formation.

We may write this mathematically using the stoichiometric numbers as:

$$\Delta H_T^\circ = \sum v_i H_{T,i}^\circ = \sum v_i \Delta H_{fT,i}^\circ = \sum_{\text{products}} |v_i| \Delta H_{fT,i}^\circ - \sum_{\text{reactants}} |v_i| \Delta H_{fT,i}^\circ \quad 3.43$$

$$\Delta H_T^{\circ} = \Delta H_R^{\circ} + \int_{T_R}^T \Delta C_P dT \quad 3.44$$

$$\Delta C_P = \sum_i \nu_i C_{P,i}$$

$$\Delta H_R^{\circ} = \sum \nu_i H_{R,i}^{\circ} = \sum \nu_i \Delta H_{fR,i}^{\circ} = \sum_{\text{products}} |\nu_i| \Delta H_{fR,i}^{\circ} - \sum_{\text{reactants}} |\nu_i| \Delta H_{fR,i}^{\circ} \quad 3.45$$

state. Almost always, the best reference state to use is $T_R = 298.15$ K and 1 bar, because this is the temperature where the standard state enthalpies (heats) of formation are commonly tabulated. The heat of formation is taken as zero for elements that naturally exist as molecules at 298.15 K and 1 bar. Then the zero value is set for the **state of aggregation** naturally occurring at 298.15 K and 1 bar. For example, H exists naturally as $\text{H}_{2(g)}$, so $\Delta H_{f,298.15}^{\circ}$ is zero for $\text{H}_{2(g)}$. Carbon is a solid, so the value of $\Delta H_{f,298.15}^{\circ}$ is zero for $\text{C}_{(s)}$. The zero values for elements in the naturally occurring state are often omitted in the tables in reference books. Enthalpies of formation are tabulated for many compounds in Appendix E at 298.15 K and 1 bar.

Energy Balances for Reactions

consider a single inlet stream and single outlet stream flowing at steady state:

$$0 = H^{in} \dot{n}^{in} - H^{out} \dot{n}^{out} + \dot{Q} + \dot{W}_S \quad 3.47$$

Heat of Reaction method replaces the first two terms in Eqn. 3.47 with the negative sum of the three steps shown by dashed lines in Fig. 3.5(a). In contrast, the **Heat of Formation method** uses an elemental reference state for every component, and the enthalpies of each component include the heat of formation as illustrated by each branch of Fig 3.5(b). The difference of enthalpies of the components then includes the generalized steps of Fig. 3.4, and the heat of reaction is included

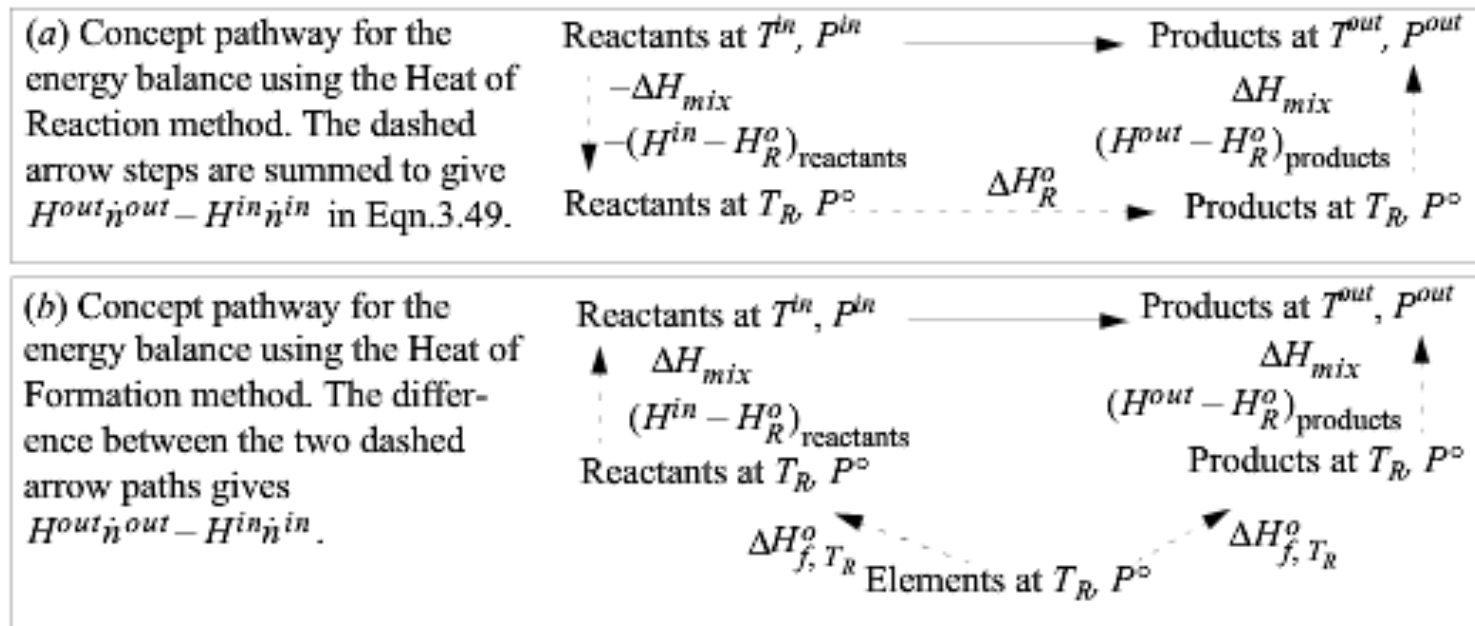


Figure 3.5 Concept pathways for (a) the Heat of Reaction method and (b) the Heat of Formation method. Details for the steps are omitted as discussed in the text.

Enthalpy of a mixed stream where there are no phase changes between T_R and T .

$$\sum_i \dot{n}_i (H - H_R^o)_i + \overset{\text{small}}{\dot{n} \Delta H_{mix}} = \sum_i \dot{n}_i \left(\int_{T_R}^T \left(\frac{\partial H}{\partial T} \right)_{P^o, i} dT + \overset{\text{usually small}}{\int_{P^o}^P \left(\frac{\partial H}{\partial P} \right)_{T, i} dP} \right) + \overset{\text{small}}{\dot{n} \Delta H_{mix}} - \sum_i \dot{n}_i \left(\int_{T_R}^T C_P dT \right) \quad 3.48$$

It might not be immediately obvious that Eqn. 3.47 includes the heat of reaction. Considering *just the flow terms of the energy balance*, by plugging Eqn. 3.48 into Eqn. 3.47 the flow terms become

$$\begin{aligned} H^{in} \dot{n}^{in} - H^{out} \dot{n}^{out} &= \sum_{\text{components}} (\dot{n}_i^{in} - \dot{n}_i^{out}) H_{i,R}^o + \\ &\sum_{\text{components}} \dot{n}_i^{in} (H^{in} - H_R^o)_i - \sum_{\text{components}} \dot{n}_i^{out} (H^{out} - H_R^o)_i \end{aligned} \quad 3.49$$

where the inlet temperature of all reactants is the same. The first term on the right of Eqn. 3.49 can be related to the heat of reaction using Eqn. 3.41 to introduce ξ and Eqn. 3.45 to insert the heat of reaction:

$$\sum_{\text{components}} (\dot{n}_i^{in} - \dot{n}_i^{out}) H_{i,R}^o = -\dot{\xi} \sum_{\text{components}} \nu_i H_{i,R}^o = -\dot{\xi} (\Delta H_R^o) \quad 3.50$$

Therefore, the steady-state energy balance can be calculated using Eqn 3.51 and the balance is known as the Heat of Reaction method:

$$0 = \sum_{\text{components}} \dot{n}_i^{in} (H^{in} - H_R^o)_i - \sum_{\text{components}} \dot{n}_i^{out} (H^{out} - H_R^o)_i + \dot{Q} + \dot{W}_S - \dot{\xi} \Delta H_R^o \quad 3.51$$

! Enthalpy of a mixed stream where there are no phase changes between T_R and T using the Heat of Formation method.

phase transitions between the reference state and the stream state looks like this:

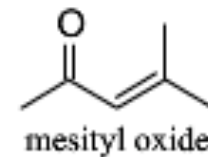
$$\sum_i \dot{n}_i [(H - H_R^o) + \Delta H_{f, T_R}^o] + \dot{n} \overset{\text{small}}{\Delta H_{mix}} - \sum_i \dot{n}_i \left(\int_{T_R}^T C_p dT + \Delta H_{f, T_R}^o \right) \quad 3.52$$

When phase changes are involved, the steps along the pathway are included as illustrated by several examples in Fig. Fig. 2.6 on page 65.

Work Effects

Example 3.6 Reactor energy balances

Acetone (A) is reacted in the liquid phase over a heterogeneous acid catalyst to form mesityl oxide (MO) and water (W) at 80°C and 0.25 MPa. The reaction is $2A \rightleftharpoons MO + W$. Conversion is to be 80%. The heat capacity of mesityl oxide has been estimated to be C_p^L (J/mol-K) = 131.16 + 0.2710T(K), C_p^V (J/mol-K) = 72.429 + 0.2645T(K), and the acentric factor is estimated to be 0.356. Other properties can be obtained from Appendix E or webbook.nist.gov. Ignore pressure corrections and assume ideal solutions.



- Estimate the heat duty for a steady-state reaction with liquid feed (100 mol/h) and liquid products. Use the Heat of Reaction method calculated using liquid heats of formation.
- Estimate the heat duty for the same conditions as (a), but use the Heat of Formation method incorporating heats of formation of ideal gases and Eqn 2.45 to estimate heat of vaporization. (This method is used by process simulators.)
- Repeat part (b) with the modification of using the experimental heat of vaporization.
- Estimate the heat duty for the same conditions as (a), but use the Heat of Formation method incorporating the heat of formation of liquids.

Example 3.6 Reactor energy balances (Continued)

Solution:

(a) For MO and A, $\Delta H_{f,298.15}^{oL} = -221, -249.4$ kJ/mol respectively, from NIST. The liquid phase standard state heat of reaction is $-221 - 285.8 - 2(-249.4) = -8$ kJ/mol. Using a reference state of the liquid species at 298.15 K and 1 bar, the enthalpy of the each component is given by

$\int_{298.15}^{353.15} C_p^L dT$; the results are {A, 7.265 kJ/mol}, {MO, 12.068}, {W, 4.161}. The mass balance

for 100 mol/h A feed and 80% conversion gives an outlet of $100(1 - 0.8) = 20$ mol/h A, then, $(\dot{n}_A^{out} = 20 = 100 - 2\dot{\xi}) \Rightarrow \dot{\xi} = 40$, $\dot{n}_{MO}^{out} = \dot{n}_W^{out} = \dot{\xi} = 40$. The energy balance is

$$\dot{Q} = \sum_{\text{components}} \dot{n}_i^{out} (H_i^{out} - H_{R,i}^o) - \sum_{\text{components}} \dot{n}_i^{in} (H_i^{in} - H_{R,i}^o) + \dot{\xi} \Delta H_R^o, \text{ or}$$

$$\dot{Q} = (20(7.265) + 40(12.068) + 40(4.161)) - 100(7.265) + 40(-8) = -252 \text{ kJ/h.}$$

(b) The value of $\dot{\xi} = 40$ is the same. The path to calculate the component liquid enthalpies using the heat of formation for ideal gases is: form ideal gas at 298.15K \rightarrow heat ideal gas to 353.15K \rightarrow condense ideal gas at 353.15K (using Eqn. 2.45). For MO $\Delta H_{f,298.15}^{oV} = -178.3$ kJ/mol, from NIST. The enthalpies of each component will be tabulated for each of the three steps: (A) $-215.7 + 4.320 - 27.71 = -239.1$ kJ/mol; (MO) $-178.3 + 8.72 - 39.0 = -208.6$ kJ/mol; (W) $-241.8 + 1.86 - 42.7 = -282.6$ kJ/mol. The energy balance is

$$\begin{aligned} \dot{Q} &= \sum_{\text{components}} \dot{n}_i^{out} H_i^{out} - \sum_{\text{components}} \dot{n}_i^{in} H_i^{in} \\ &= (20(-239.1) + 40(-208.6) + 40(-282.6)) - 100(-239.1) = -520 \text{ kJ/h.} \end{aligned}$$

In principle, this method should have given the same result as (a), but the value differs significantly. The method is sensitive to the accuracy of the prediction for the heat of vaporization. When this method is used, the accuracy of the heat of vaporization needs to be carefully evaluated.

(c) To evaluate the effect of the prediction of the heat of vaporization, let us repeat with a modified path through the normal boiling point of the species, using the experimental heat of vaporization. The normal boiling point of MO from NIST is 403 K, and $\Delta H^{vap} = 42.7$ kJ/mol. The component enthalpy path is modified to: form ideal gas at 298.15 K \rightarrow heat ideal gas to $T_b \rightarrow$ condense to liquid at $T_b \rightarrow$ change liquid to 353.15 K. The enthalpies of each step and totals are: (A) $-215.7 + 2.4 - 30.2 + 3.3 = -240.2$ kJ/mol; (MO) $-178.3 + 17.3 - 42.7 - 11.6 = -215.3$ kJ/mol; (W) $-241.9 + 2.5 - 40.7 - 1.5 = -281.6$ kJ/mol. The energy balance is

$$\dot{Q} = (20(-240.2) + 40(-215.3) + 40(-281.6)) - 100(-240.2) = -660 \text{ kJ/h.}$$

Parts (b) - (c) result in different heat transfer compared to (a). Note the difference in the heat of formation of vapor and liquid MO at 25°C matches the heat of vaporization at the normal boiling point and the difference would be expected to be larger. The original references for the thermochemical data should be consulted to decide which is most reliable.

Example 3.6 Reactor energy balances (Continued)

(d) This modification will not require heats of vaporization. The component enthalpy path is: form liquid at 298.15 K and heat liquid to 353.15 K. The sensible heat calculations are the same as tabulated in part (a). The enthalpies for the two steps and sum for each component are:

(A) $-249.4 + 7.265 = -242.1$ kJ/mol; (MO) $-221 + 12.068 = -208.9$; (W) $-285.8 + 4.2 = -281.6$.

The energy balance becomes:

$$\dot{Q} = (20(-242.1) + 40(-208.9) + 40(-281.6)) - 100(-242.1) = -252 \text{ kJ/h}$$

Comparing with (a), the Heat of Formation method and the Heat of Reaction method give the same results when the same properties are used.