Rudolf Clausius

Sadi Carnot

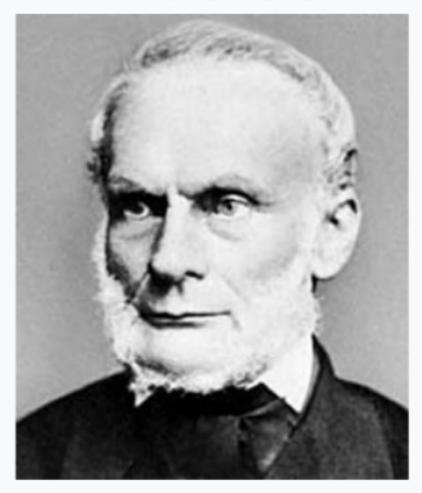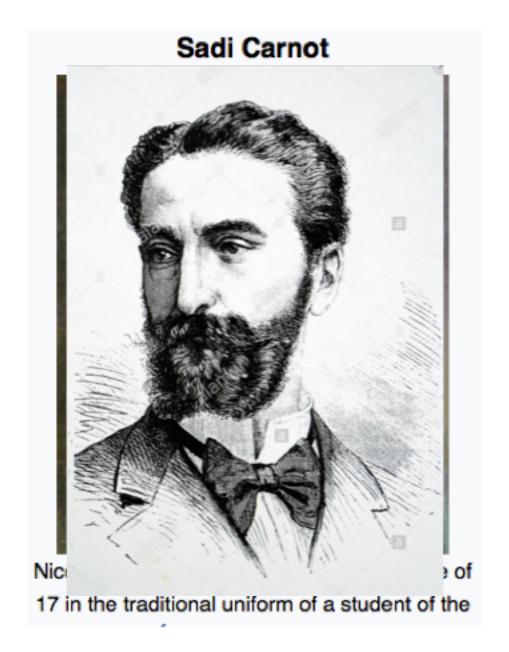Nic... ...e of 17 in the traditional uniform of a student of the

ENTROPY

$$S = k \ln W$$

L. Boltzmann

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.

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

4.1

where $d\underline{S}$ is the entropy change of the system. We will later show that this definition is consistent with the microscopic definition.

Microscopic definition—Entropy is a measure of the molecular disorder of the system. Its value is related to the number of microscopic states available at a particular macroscopic state. Specifically, for a system of fixed energy and number of particles, N,

$$\underline{S}_i \equiv k\ln(p_i) \quad \text{or} \quad \Delta\underline{S} \equiv k\ln\left(\frac{p_2}{p_1}\right)$$

4.2

where p_i is the number of microstates in the ith macrostate, $k = R/N_A$. We define microstates and macrostates in the next section.
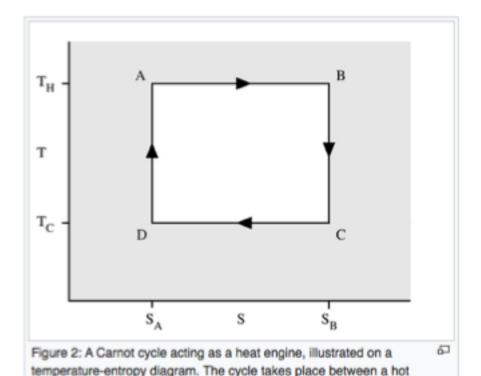
For a single state $\ln(1) = 0$. At absolute 0, in a perfect crystal with no defects etc.

Entropy of different aspects of a system, conformational entropy, translational entropy

A contribution to energy that is linear in temperature

4

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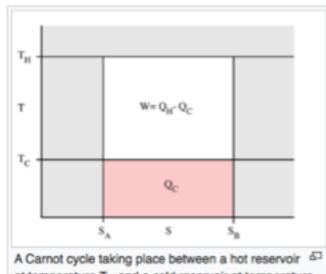
$$dS \equiv \frac{dQ_{rev}}{T_{sys}}$$

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.

Constant Temperature (Isothermal) Pathway

The behavior of entropy at constant temperature is more difficult to generalize in the absence of charts and tables because dQ_{rev} depends on the state of aggregation. For the ideal gas, $dU = 0 = dQ - PdV$, $dQ = RTdV/V$, and plugging into Eqn. 4.13,

Isothermal.

$$\Delta S^{ig} = R \ln\left[\frac{V_2}{V_1}\right] \quad \text{or} \quad \Delta S^{ig} = -R \ln\left[\frac{P_2}{P_1}\right] \qquad \text{(ig) 4.22}$$

For a liquid or solid, the effect of isothermal pressure of volume change is small as a first approximation; the precise relations for detailed calculations will be developed in Chapters 6–8. Looking at the steam tables at constant temperature, entropy is very weakly dependent on pressure for *liquid* water. This result may be generalized to other liquids below $T_r = 0.75$ and also to solids. For *condensed* phases, to a first approximation, entropy can be assumed to be independent of pressure (or volume) at *fixed temperature*.
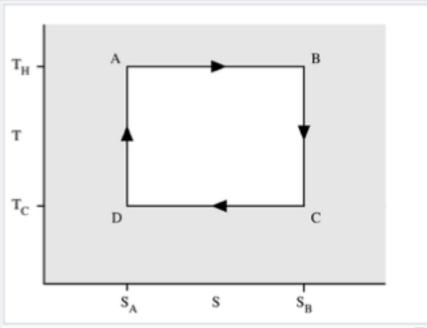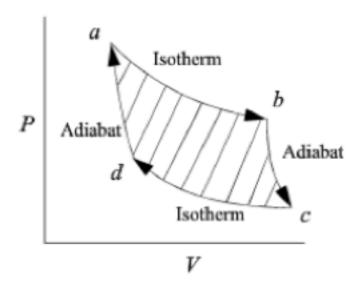

Figure 2: A Carnot cycle acting as a heat engine, illustrated on a temperature-entropy diagram. The cycle takes place between a hot reservoir at temperature T_H and a cold reservoir at temperature T_C. The vertical axis is temperature, the horizontal axis is entropy.

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

6

Entropy and Spatial Distributions: Configurational Entropy

Figure 4.1 *Illustration of configurational arrangements of two molecules in two boxes, showing the microstates. Not that β and γ would have the same macroscopic value of pressure.*

between zero, one, and two particles in a box, but could not distinguish *which* particles are present. Therefore, microstates α and δ are different macrostates because the distribution of particles is different; however, microstates β and γ give the same macrostate. Thus, from our four microstates, we have only three macrostates.

Table 4.1 *Illustration of Macrostates for Two Particles and Two Boxes*

Macrostate		# of microstates	Probability of macrostate
# in box A	# in box B		
0	2	1	0.25
1	1	2	0.5
2	0	1	0.25

What happens when we consider more particles? It turns out that the total number of microstates for N particles in M boxes is M^N, so the counting gets tedious. For five particles in two

Table 4.2 *Microstates for the Second and Third Macrostates for Five Particles Distributed in Two Boxes*

(a) One particle in Box A		(b) Two particles in Box A			
Box A	**Box B**	**Box A**	**Box B**	**Box A**	**Box B**
1	2,3,4,5	1,2	3,4,5	2,4	1,3,5
2	1,3,4,5	1,3	2,4,5	2,5	1,3,4
3	1,2,4,5	1,4	2,3,5	3,4	1,2,5
4	1,2,3,5	1,5	2,3,4	3,5	1,2,4
5	1,2,3,4	2,3	1,4,5	4,5	1,2,3

There are $M^N = 2^5 = 32$ microstates

Macrostate		# Microstates	Probability of Macrostate
Box A	**Box B**		
0	5	1	0.0313
1	4	5	0.1563
2	3	10	0.3125
3	2	10	0.3125
4	1	5	0.1563
5	0	1	0.0313

$$p_j = \frac{N_j!}{\displaystyle\prod_{i=1}^{M} m_{ij}!}$$

4.4 ❗ General for-
mula for number of
microstates for N
particles in M
boxes.

m_{ij} is the number of particles in the ith box at the jth macrostate.

microstates for arranging N particles in two boxes, with m particles in one of the boxes, is:[9]

$$p_j = \frac{N_j!}{m_j!(N_j - m_j)!}$$

4.3

Entropy and Isothermal Volume/Pressure Change for Ideal Gases

Suppose an insulated container, partitioned into two equal volumes, contains N molecules of an ideal gas in one section and no molecules in the other. When the partition is withdrawn, the molecules quickly distribute themselves uniformly throughout the total volume. How is the entropy affected? Let subscript 1 denote the initial state and subscript 2 denote the final state. Here we take for granted that the final state will be evenly distributed.

We can develop an answer by applying Eqn. 4.4, and noting that $0! = 1$:

$$p_1 = \frac{N!}{N!\,0!} = 1; \qquad p_2 = \frac{N!}{(N/2)!(N/2)!}; \qquad \ln(p_2/p_1) = \ln\left(\frac{N!/[(N/2)!]^2}{1}\right)$$

Substituting into Eqn. 4.2, and recognizing $\ln\left[\left(\frac{N}{2}\right)!\right]^2 = 2\ln\left(\frac{N}{2}\right)!$,

$$\Delta \underline{S} = \underline{S}_2 - \underline{S}_1 = k\ln(p_2/p_1) = k\{\ln(N!) - 2\ln[(N/2)!]\}$$

Stirling's approximation may be used for $\ln(N!)$ when $N > 100$,

$$\boxed{\ln(N!) \approx N\ln(N) - N} \tag{4.5}$$

The approximation is a mathematical simplification, and not, in itself, related to thermodynamics.

$$\Rightarrow \Delta\underline{S} = k[N\ln(N) - N - 2(N/2)\ln(N/2) + 2(N/2)]$$
$$= k[N\ln(N) - N - N\ln(N) + N\ln(2) + N]$$
$$= kN\ln(2) \Rightarrow \Delta\underline{S} = nR\ln(2)$$

Therefore, entropy of the system has increased by a factor of ln(2) when the volume has doubled at constant T. Suppose the box initially with particles is three times as large as the empty box. In this case the increase in volume will be 33%. Then what is the entropy change? The trick is to imagine four equal size boxes, with three equally filled at the beginning.

$$p_1 = \frac{N!}{[(N/3)!]^3 0!}; \qquad p_2 = \frac{N!}{[(N/4)!]^4}$$

A similar application of Stirling's approximation gives,

$$\Delta S = k\ln\left\{ \frac{N!}{[(N/4)!]^4} \cdot \frac{[(N/3)!]^3 0! \, 11}{N!} \right\} = -k\left\{ N\ln\left(\frac{N}{4}\right) - N - N\ln\left(\frac{N}{3}\right) + N \right\} = nR\ln\left(\frac{4}{3}\right)$$

We may generalize the result by noting the pattern with this result and the previous result,

$$(\Delta S)_T = R\ln\left[\frac{V}{V^j}\right] \qquad\qquad \text{(ig) 4.6}$$

where the subscript T indicates that this equation holds at constant T. For an isothermal ideal gas, we also may express this in terms of pressure by substituting $V = RT/P$ in Eqn. 4.6

$$(\Delta S)_T = -R\ln\left[\frac{P}{P^j}\right] \qquad\qquad \text{(ig) 4.7}$$

Example 4.1 Entropy change and "lost work" in a gas expansion

An isothermal ideal gas expansion produces maximum work if carried out reversibly and less work if friction or other losses are present. One way of generating "other losses" is if the force of the gas on the piston is not balanced with the opposing force during the expansion, as shown in part (b) below. Consider a piston/cylinder containing one mole of nitrogen at 5 bars and 300 K is expanded isothermally to 1 bar.

(a) Suppose that the expansion is reversible. How much work could be obtained and how much heat is transferred? What is the entropy change of the gas?

(b) Suppose the isothermal expansion is carried out irreversibly by removing a piston stop and expanding against the atmosphere at 1 bar. Suppose that heat transfer is provided to permit this to occur isothermally. How much work is done by the gas and how much heat is transferred? What is the entropy change of the gas? How much work is lost compared to a reversible isothermal process and what percent of the reversible work is obtained (the efficiency)?

Solution:
Basis: 1 mole, closed unsteady-state system.

(a) The energy balance for the piston/cylinder is $\Delta U = Q + W_{EC} = 0$ because the gas is isothermal and ideal. $dW_{EC} = -PdV = -(nRT/V)dV$; $W_{EC} = -nRT\ln(V_2/V_1) = -nRT\ln(P_1/P_2) = -(1)8.314(300)\ln(5) = -4014J$. By the energy balance $Q = 4014J$.
The entropy change is by Eqn. 4.7, $\Delta S = -nR\ln(P_2/P_1) = -(1)8.314\ln(1/5) = 13.38$ J/K.

(b) The energy balance does not depend on whether the work is reversible and is the same.
Taking the atmosphere as the system, the work is $W_{EC,atm} = -P_{atm}(V_{2,atm}-V_{1,atm}) = -W_{EC} = -P_{atm}(V_1-V_2) = P_{atm}(nRT/P_2-nRT/P_1) = nRT(P_{atm}/P_2-P_{atm}/P_1) =>$
$W_{EC} = nRT(P_{atm}/P_1-P_{atm}/P_2) = (1)8.314(300)(1/5-1) = -1995J$, $Q = 1995J$.
The entropy change depends on only the state change and this is the same as (a), 13.38 J/K.
The amount of lost work is $W_{lost} = 4014 - 1995 = 2019J$, the percent of reversible work obtained (efficiency) is $1995/4014 \cdot 100\% = 49.7\%$.

Entropy of Mixing for Ideal Gases

Mixing is another important process to which we may apply the statistics that we have developed. Suppose that one mole of pure oxygen vapor and three moles of pure nitrogen vapor at the same temperature and pressure are brought into intimate contact and held in this fashion until the nitrogen and oxygen have completely mixed. The resultant vapor is a uniform, random mixture of nitrogen and oxygen molecules. Let us determine the entropy change associated with this mixing process, assuming ideal-gas behavior.

Since the T^i and P^i of both ideal gases are the same, $V^i_{N2} = 3V^i_{O2}$ and $V^i_{tot} = 4V^i_{O2}$. Ideal gas molecules are point masses, so the presence of O_2 in the N_2 does not affect anything as long as the pressure is constant. The main effect is that the O_2 now has a larger volume to access and so does N_2. The component contributions of entropy change versus volume change can be simply added. Entropy change for O_2:

$$\Delta S = n_{O2}R\ln(4) = n_{tot}R[-x_{O2}\ln(0.25)] = n_{tot}R[-x_{O2}\ln(x_{O2})]$$

Entropy change for N_2:

$$\Delta S = n_{N2}R\ln\left(\frac{4}{3}\right) = n_{tot}R[-x_{N2}\ln(0.75)] = n_{tot}R[-x_{N2}\ln(x_{N2})]$$

Entropy change for total fluid:

$$\Delta S = -n_{tot}R[x_{O2}\ln(x_{O2}) + x_{N2}\ln(x_{N2})] = -4R(-0.562) = 18.7 \text{ J/K}$$

$$\boxed{\Delta S^{is}_{mix} = -R\sum_i x_i\ln x_i} \quad \textit{In general, ideal mixing.} \qquad 4.8$$

The entropy of a mixed ideal gas or an **ideal solution**, here both denoted with a superscript *"is:"*

$$\boxed{S^{is} = \sum_i n_iS_i + \Delta S_{mix} = \sum_i n_iS_i - R\sum_i n_i\ln x_i} \text{ or } \boxed{S^{is} = \sum_i x_iS_i - R\sum_i x_i\ln x_i} \qquad 4.9$$

4.3   THE MACROSCOPIC VIEW OF ENTROPY

Molar or specific entropy is a *state* property which will assist us in the following ways.

1. Irreversible processes will result in an increase in entropy of the *universe*. (Irreversible processes will result in entropy generation.) Irreversible processes result in loss of capability for performing work.

2. Reversible processes result in no increase in entropy of the *universe*. (Reversible processes result in zero entropy generation. This principle will be useful for calculation of maximum work output or minimum work input for a process.)

3. Proposed processes which would result in a decrease of entropy of the universe are impossible. (Impossible processes result in negative entropy generation.)

Defines "reversible" as $\Delta S = 0$
Defines "impossible" as self-organizing;
        $\Delta S < 0$ with no energy input

Allows Calculation of Effeciency
S=0 process has no waste energy (heat)
Actually process has waste energy
Ratio of Wwith waste/S=0 work = effeciency

Entropy Definition (Macroscopic)

Let us define the differential change in entropy of a *closed* simple system by the following equation:

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

4.12

For a change in states, both sides of Eqn. 4.12 may be integrated,

$$\Delta S = \int_{state\ 1}^{state\ 2} \frac{dQ_{rev}}{T_{sys}}$$

4.13

where the following occurs:

1. The entropy change on the left-hand side of Eqn. 4.13 is dependent only on states 1 and 2 and not dependent on reversibility. However, to calculate the entropy change via the integral, the *integral* may be evaluated along any convenient *reversible* pathway between the actual states.

2. T_{sys} is the temperature of the system boundary where heat is transferred. Only if the system boundary temperature is constant along the pathway may this term be taken out of the integral sign.

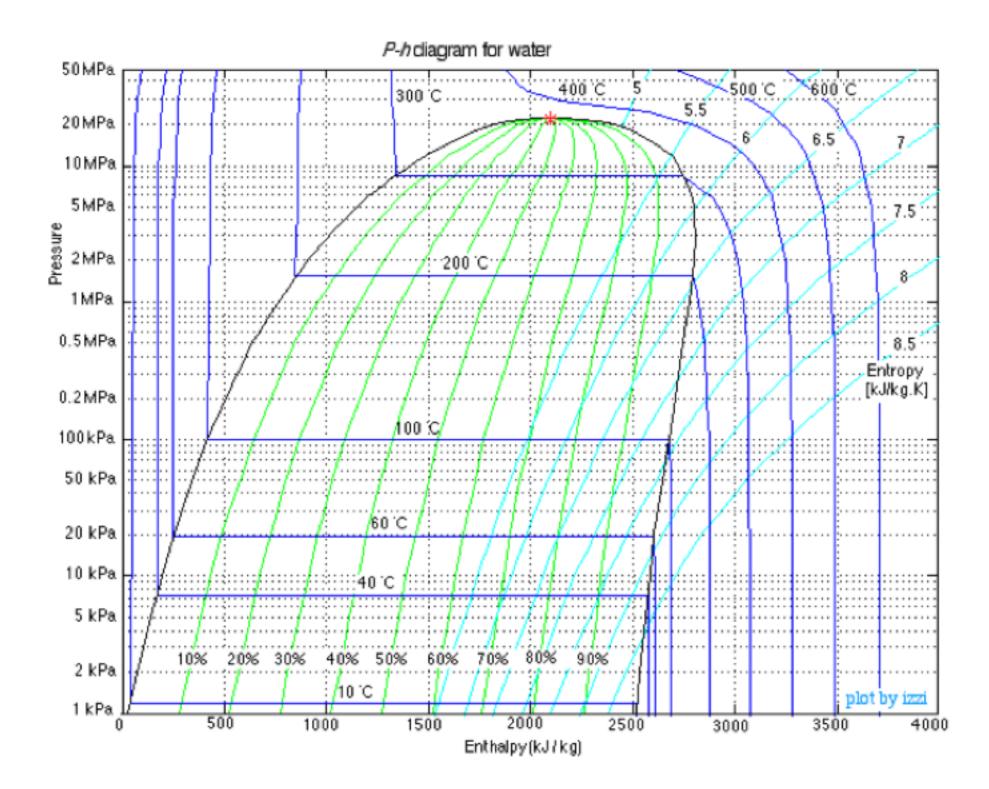## Example 4.3 Adiabatic, reversible expansion of steam

Steam is held at 450°C and 4.5 MPa in a piston/cylinder. The piston is adiabatically and reversibly expanded to 2.0 MPa. What is the final temperature? How much reversible work can be done?
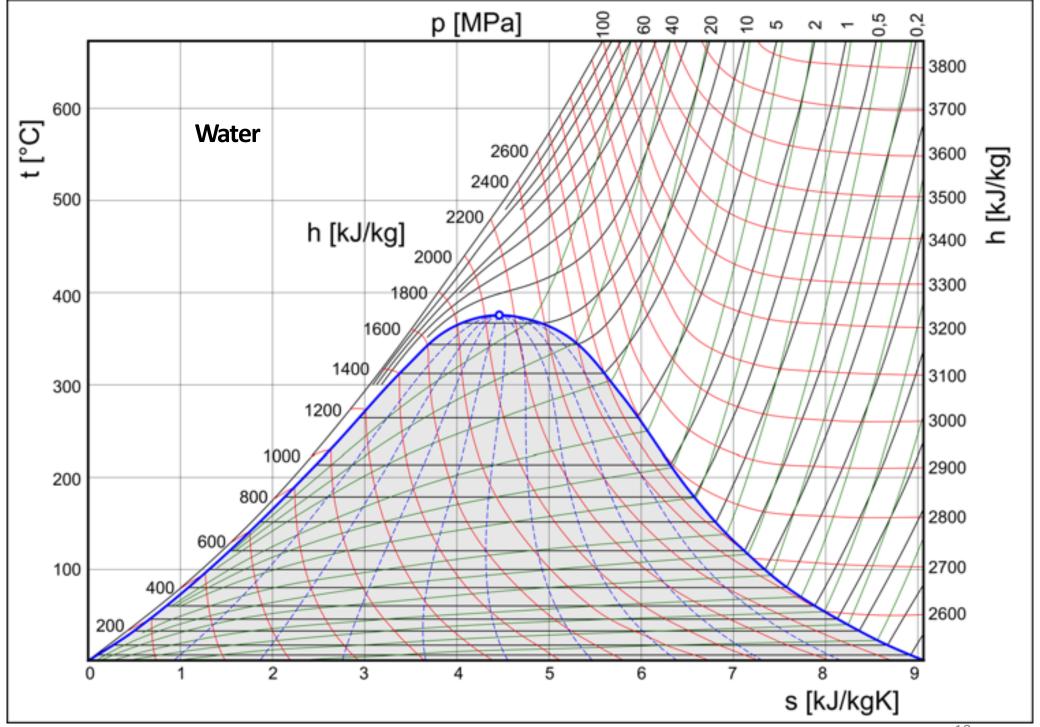
Solution: The T, P are known in the initial state, and the value of S can be found in the steam tables. Steam is not an ideal gas, but by Eqn. 4.12, the process is isentropic because it is reversible and adiabatic. From the steam tables, the entropy at the initial state is 6.877 kJ/kgK. At 2 MPa, this entropy will be found between 300°C and 350°C. Interpolating,

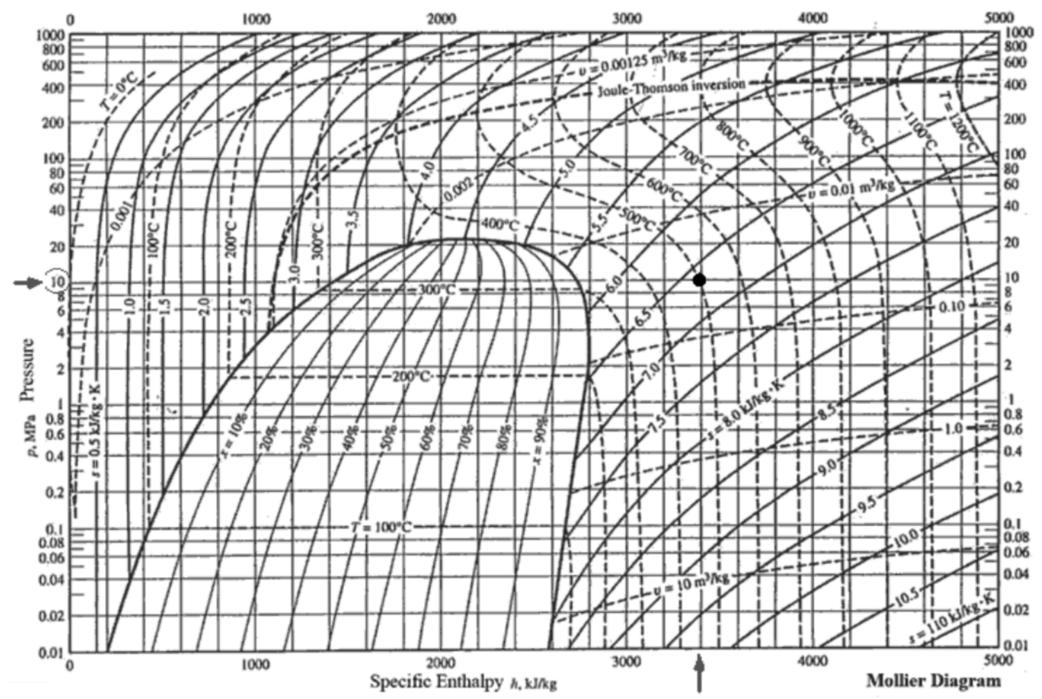$$T = 300 + \frac{6.877 - 6.7684}{6.9583 - 6.7684}(350 - 300) = 300 + 0.572(350 - 300) = 329°C$$

The P and $S^f = S^i$ are known in the final state and these two state properties can be used to find all the other final state properties. The work is determined by the energy balance: $\Delta U = Q + W_{EC}$. The initial value of U is 3005.8 kJ/kg. For the final state, interpolating U by using S^f at P^f, $U = 2773.2 + 0.572(2860.5 - 2773.2) = 2823.1$ kJ/kg, so

$$W_{EC} = (2823.1 - 3005.8) = -182.7 \text{ kJ/kg}$$

P-h diagram for water

Water

Mollier Diagram

Specific Enthalpy h, kJ/kg

p, MPa Pressure

Mollier-h, s Diagram

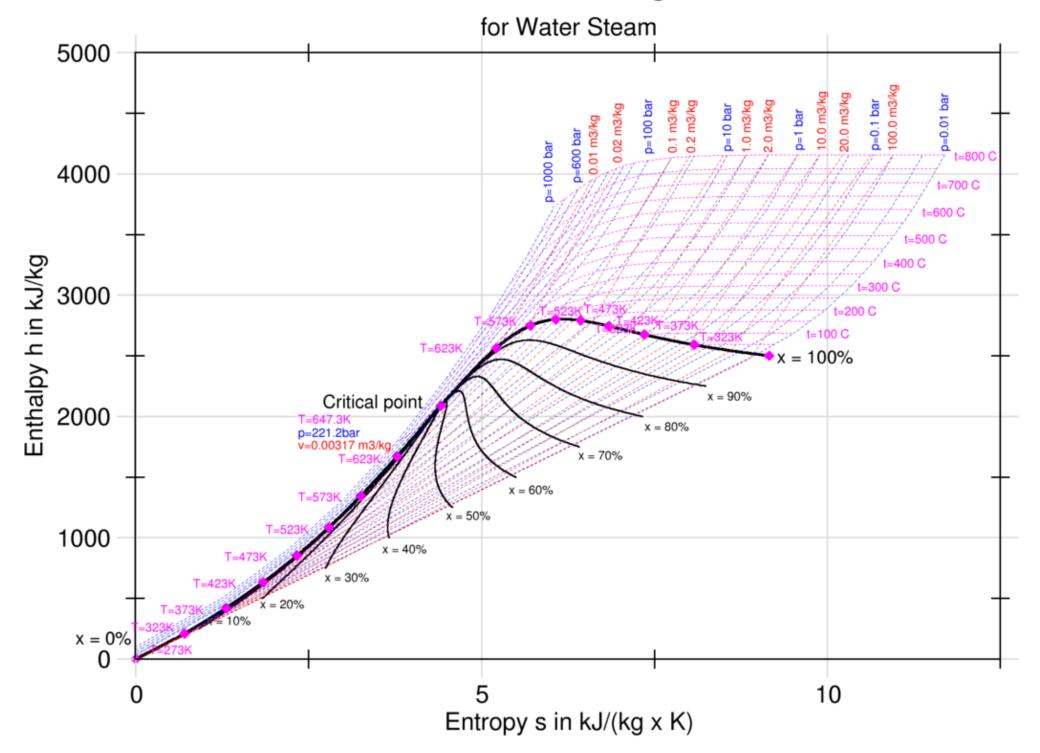## for Water Steam

Let us revisit the Carnot cycle of Section 3.1 in light of this new state property, entropy. The Carnot cycle was developed with an ideal gas, but it is possible to prove that the cycle depends only on the combination of two isothermal steps and two adiabatic steps, not the ideal gas as the working fluid.[14] Because the process is cyclic, the final state and initial state are identical, so the overall entropy changes of the four steps must sum to zero, $\Delta S = 0$. Because the reversible, adiabatic steps are isentropic, $\Delta S = 0$, the entropy change for the two isothermal steps must sum to zero. As we discussed above, for an isothermal step Eqn. 4.13 becomes $\Delta S = Q_{rev}/T$. Therefore, an analysis of the Carnot cycle from the viewpoint of entropy is
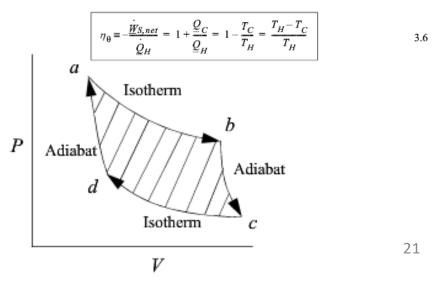
$$\left(\Delta S = 0 = \frac{Q_H}{T_H} + \frac{Q_C}{T_C}\right) \Rightarrow \frac{Q_C}{Q_H} = \frac{-T_C}{T_H} \quad \text{Carnot cycle} \qquad 4.14$$

This can be inserted into the formula for Carnot efficiency, Eqn. 3.6. Note that this relation is not constrained to an ideal gas! In fact, there are only three constraints for this balance: The process is cyclic; all heat is absorbed at T_H; all heat is rejected at T_C. Example 4.4 shows how the Carnot cycle can be performed with steam including phase transformations.

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.

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

Rules for Carnot Cycle

Isothermal
    (vary P) $Q = -W_{EC} = -nRT\ln(V_2/V_1)$

Isothermal
    Isobaric $Q = \Delta U - W_{EC} = \Delta U + P\Delta V = \Delta H$
                         $W_{EC} = -P\Delta V$

Adiabatic
    Reversible $Q = 0 \quad \Delta S = 0$
                 $W_{EC} = \Delta U = R\, C_V\, (T_2 - T_1)$

For Turbine
    The work done by the gas is work done by the turbine (blades moved around by the gas) plus the work done by pressures (flow work).

$$U_2 - U_1 = -W_{shaft} + P_1 V_1 - P_2 V_2 \quad \text{(adiabatic turbine)}$$

$$-W_{shaft} = H_2 - H_1$$

Difference between shaft work and expansion/contraction work

Example 4.4 A Carnot cycle based on steam

Fig. 4.3 shows the path of a Carnot cycle operating on steam in a continuous cycle that parallel the two isothermal steps and two adiabatic steps of Section 3.1. First, saturated liquid at 5 MPa is boiled isothermally to saturated vapor in step $(a{\to}b)$. In step $(b{\to}c)$, steam is adiabatically and reversibly expanded from saturated vapor at 5 MPa to 1 MPa. In $(c{\to}d)$, heat is isothermally removed and the volume drops during condensation. Finally, in step $(d{\to}a)$, the steam is adiabatically and reversibly compressed to 5 MPa and saturated liquid. (Hint: Challenge yourself to solve the cycle without looking at the solution.).

(a) Compute $W(a{\to}b)$ and Q_H.
(b) Compute $W(b{\to}c)$.
(c) Compute $W(d{\to}a)$. (The last step in the cycle).
(d) Compute $W(c{\to}d)$ and Q_C (The third step in the cycle).
(e) For the cycle, compute the thermal efficiency by $\eta_\theta = -W_{net}/Q_H$ and compare to Carnot's efficiency, $\eta_\theta = (T_H - T_L)/T_H$.
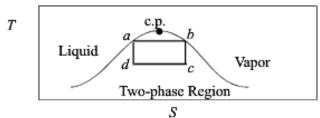

Figure 4.3 *A T-S diagram illustrating a Carnot cycle based on steam.*

Solution: The entropy change is zero for the expansion and compression steps because these steps are adiabatic and reversible, as indicated by the vertical line segments in Fig. 4.3.

(a) E-balance: fixed P,T vaporization, $Q_H = \Delta U - W_{EC} = (\Delta U + P\Delta V) = \Delta H^{vap} = 1639.57$ J/kg;
$W_{EC}(a{\to}b) = P\Delta V = 5(0.0394 - 0.001186)*1000 = 191.1$ J/kg.

(b) E-balance: isentropic, $W_{EC}(b{\to}c) = \Delta U$; $U_b = U$(sat. vap., 5MPa) = 2596.98 kJ/kg;
S-balance: $\Delta S = 0$; $S_c = S_b = 5.9737$ kJ/kg-K$= q_c(6.5850) + (1 - q_c)2.1381$; $q_c = 0.8625$;
$U_c = 0.8625(2582.75) + (1 - 0.8625)761.39 = 2332.31$ kJ/kg;
$W_{EC}(b{\to}c) = 2332.31 - 2596.98 = -264.67$ kJ/kg.

(c) This is the last step. E-balance: isentropic. $W_{EC}(d{\to}a) = \Delta U$; $U_d = U$(sat. liq., 5MPa) = 1148.21 kJ/kg; the quality at state d is not known, but we can use the entropy at state a to find it.
S-balance: $\Delta S = 0$; $S_d = S_a = 2.9210$ kJ/kg-K$= q_d(6.5850) + (1 - q_d)2.1381$; $q_d = 0.1761$;
$U_d = 0.1761(2582.75) + (1 - 0.1761)761.39 = 1082.13$ kJ/kg;
$W_{EC}(d{\to}a) = 1082.13 - 1148.21 = -66.08$ kJ/kg.

Example 4.4 A Carnot cycle based on steam (Continued)

(d) This is the third step using the quality for d calculated in part (c). This is a fixed T,P condensation. E-balance: $Q_C = \Delta U - W_{EC} = (\Delta U + P\Delta V) = \Delta H$; $H_d = 762.52 + 0.1761(2014.59) = 1117.29$ kJ/kg; $H_c = 762.52 + 0.8625(2014.59) = 2500.10$ kJ/kg; $Q_C = H_d - H_c = -1382.21$ kJ/kg $W_{EC} = P\Delta V$; $V_c = 0.001127(1 - 0.8625) + 0.8625(0.1944) = 0.1678$ m^3/kg $= 167.8$ cm^3/g $V_d = 0.001127(1 - 0.1761) + 0.1761(0.1944) = 0.0352$ m^3/kg $= 35.2$ cm^3/g $W(c \rightarrow d) = 1.0(35.2 - 167.8) = -132.6$ MPa-cm^3/g $= -132.6$ kJ/kg

(e) $\eta_\theta = -W_{net}/Q_H$; $W_{net} = (264.67 - 66.08 + 191.1 - 132.6) = 257.1$ kJ/kg; $\eta_\theta = 257.1/1639.57 = 0.157$; η_θ (Carnot) $= (263.94 - 179.88)/(263.94 + 273.15) = 0.157$. The actual cycle matches the Carnot formula. Note that the cyclic nature of this process means that we could have computed more quickly by $W_{net} = -(Q_C + Q_H) = 1382.21 - 1639.57 = 257.4$ kJ/kg.

Calculation of Entropy Changes in Closed Systems

For a closed *reversible* system without shaft work,

$$d\left[U + \frac{v^2}{2g_c} + \frac{g}{g_c}z\right] = dQ_{rev} + dW_S + dW_{EC} \qquad 4.15$$

$$[dU + PdV] = dQ_{rev} \qquad 4.16$$

Constant Pressure (Isobaric) Pathway

Many process calculations involve state changes at constant pressure. Recognizing $H = U + PV$, $dH = dU + PdV + VdP$. In the case at hand, dP happens to be zero; therefore, Eqn. 4.16 becomes

$$dH = dQ_{rev} \qquad 4.17$$

Since $dH = C_P dT$ at constant pressure, along a *constant-pressure pathway*, substituting for dQ_{rev} in Eqn. 4.13, the entropy change is

$$(dS)_P = \frac{C_P}{T}(dT)_P \qquad 4.18$$

$$\boxed{\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT} \qquad 4.19 \quad \text{❗ Constant pressure.}$$

Constant Volume Pathway

For a constant volume pathway, Eqn. 4.16 becomes

$$dU = dQ_{rev} \qquad\qquad 4.20$$

Since $dU = C_V dT$ along a *constant volume pathway*, substituting for dQ_{rev} in Eqn. 4.13, the entropy change is

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT \qquad\qquad 4.21$$

🛈 Constant volume.

Constant Temperature (Isothermal) Pathway

The behavior of entropy at constant temperature is more difficult to generalize in the absence of charts and tables because dQ_{rev} depends on the state of aggregation. For the ideal gas, $dU = 0 = dQ - PdV$, $dQ = RTdV/V$, and plugging into Eqn. 4.13,

🛈 Isothermal.

$$\Delta S^{ig} = R \ln\left[\frac{V_2}{V_1}\right] \text{ or } \Delta S^{ig} = -R \ln\left[\frac{P_2}{P_1}\right] \qquad\qquad \text{(ig) 4.22}$$

For a liquid or solid, the effect of isothermal pressure of volume change is small as a first approximation; the precise relations for detailed calculations will be developed in Chapters 6–8. Looking at the steam tables at constant temperature, entropy is very weakly dependent on pressure for *liquid* water. This result may be generalized to other liquids below $T_r = 0.75$ and also to solids. For *condensed* phases, to a first approximation, entropy can be assumed to be independent of pressure (or volume) at *fixed temperature*.

Adiabatic Pathway

A process that is adiabatic *and reversible* will result in an *isentropic path*. By Eqn. 4.13,

$$\Delta S = \int_{state\ 1}^{state\ 2} \frac{dQ_{rev}}{T_{sys}} = 0 \quad \text{for reversible process only.} \qquad 4.23$$

Note that a path that is adiabatic, but not reversible, will not be isentropic. This is because a reversible adiabatic process starting at the same state 1 will not follow the same path, so it will not end at state 2, and reversible heat transfer will be necessary to reach state 2.

Phase Transitions

In the absence of property charts or tables, entropy changes due to phase transitions can be easily calculated. Since equilibrium phase transitions for pure substances occur at constant temperature and pressure, for vaporization

$$\Delta S^{vap} = \int \frac{dQ_{rev}}{T} = \frac{1}{T^{sat}} \int dQ_{rev} = \frac{Q^{vap}}{T^{sat}}$$

where T^{sat} is the equilibrium saturation temperature. Likewise for a solid-liquid transition,

$$\Delta S^{fus} = \frac{Q^{fus}}{T_m}$$

where T_m is the equilibrium melting temperature. Since either transition occurs at constant pressure if along a reversible pathway, we may include Eqn. 4.17, giving

$$\Delta S^{vap} = \frac{\Delta H^{vap}}{T^{sat}} \quad \text{and} \quad \Delta S^{fus} = \frac{\Delta H^{fus}}{T_m} \qquad 4.24$$

Example 4.5 Ideal gas entropy changes in an adiabatic, reversible expansion

In Example 2.11 on page 75, we derived the temperature change for a closed-system adiabatic expansion of an ideal gas. How does the entropy change along this pathway, and what does this example show about changes in entropy with respect to temperature?

Solution: Reexamine the equation $(C_V/T)dT = -(R/V)dV$, which may also be written $(C_V/R)d\ln T = -d\ln V$. We can sketch this path as shown by the diagonal line in Fig. 4.4. Since our path is adiabatic $(dQ = 0)$ and reversible, and our definition of entropy is $dS = (dQ_{rev})/T$, we expect that this implies that the path is also isentropic (a constant-entropy path). Since entropy is a state property, we can verify this by calculating entropy along the other pathway of the figure consisting of a constant temperature (step A) and a constant volume (step B)

For the reversible isothermal step we have

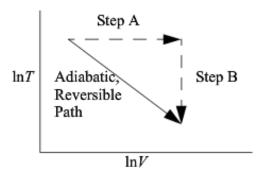$$dU = dQ_{rev} - PdV = 0 \quad \text{or} \quad dQ_{rev} = PdV \tag{ig}$$

Figure 4.4 *Equivalence of an adiabatic and an alternate path on a T-V diagram.*

Thus,

$$(dS)_T = \frac{dQ_{rev}}{T} = \frac{PdV}{T} \tag{ig}$$

Substituting the ideal gas law,

$$(dS^{ig})_T = \frac{RTdV}{VT} = R\frac{dV}{V} \tag{ig} \; 4.25$$

Example 4.5 Ideal gas entropy changes in an adiabatic, reversible expansion (Continued)

For the constant volume step, we have

$$dU = dQ_{rev} \quad \text{or} \quad C_V dT = dQ_{rev}$$

Thus,

$$(dS)_V = \frac{dQ_{rev}}{T} = C_V \frac{dT}{T} \qquad 4.26$$

We could replace a differential step along the adiabat (adiabatic pathway) with the equivalent differential steps along the alternate pathways; therefore, we can see that the change in entropy is zero,

$$dS^{ig}_{adiabat} = (dS)_V + (dS^{ig})_T = \frac{C_V}{T} dT + \frac{R}{V} dV = 0 \qquad \text{(ig) } 4.27$$

which was shown by the energy balance in Eqn. 2.62, and we verify that the overall expansion is isentropic. Trials with additional pathways would show that ΔS is the same.

The entropy change along the adiabatic, reversible path is the same as along (step A + step B) illustrating that S is a state property.

The method of subdividing state changes into individual temperature and volume changes can be generalized to any process, not just the adiabatic process of the previous example, giving

$$dS^{ig} = \frac{C_V}{T} dT + \frac{R}{V} dV \qquad \text{(ig) } 4.28$$

We may integrate steps A and B independently. We also could use temperature and pressure steps to calculate entropy changes, resulting in an alternate formula:

$$\Delta S^{ig} = C_V \ln \frac{T}{T^i} + R \ln \frac{V}{V^i} \quad \text{or} \quad \Delta S^{ig} = C_P \ln \frac{T}{T^i} - R \ln \frac{P}{P^i} \qquad \text{(*ig) } 4.29$$

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

4.30

which provides a relationship between C_V and entropy. Similarly, looking back at Eqn. 4.18,

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

4.31

Example 4.6 Ideal gas entropy change: Integrating $C_P^{ig}(T)$

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy using the ideal gas law.

Solution: Because P and T are specified in each state, the ideal gas change is calculated most easily by combining an isobaric temperature step, Eqns. 4.19, and an isothermal pressure change, Eqn. 4.22. The heat capacity constants are obtained from Appendix E.

$$S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} \frac{C_P^{ig}}{T} dT - R\ln\frac{P_2}{P_1}; \int_{T_1}^{T_2} \frac{C_P^{ig}}{T} dT = \int_{T_1}^{T_2} \frac{(A + BT + CT^2 + DT^3)}{T} dT$$

$$S_2^{ig} - S_1^{ig} = A\ln\left(\frac{T_2}{T_1}\right) + B(T_2 - T_1) + \frac{C}{2}(T_2^2 - T_1^2) + \frac{D}{3}(T_2^3 - T_1^3) - R\ln\frac{P_2}{P_1}$$

$$= -4.224\ln\frac{463.15}{378.15} + 0.3063(463.15 - 378.15) + \frac{-1.586\times10^{-4}}{2}(463.15^2$$

$$-378.15^2) + \frac{3.215\times10^{-8}}{3}(463.15^3 - 378.15^3) - 8.314\ln\frac{25}{5} = 6.613 \text{ J/mol-K}$$

Example 4.7 Entropy generation and "lost work"

In Example 4.1 consider the surroundings at 300 K: (a) Consider the entropy change in the surroundings and the universe for parts 4.1(a) and 4.1(b) and comment on the connection between entropy generation and lost work; (b) How would entropy generation be affected if the surroundings are at 310 K?

Solution:

(a) For 4.1(a) the entropy change of the surroundings is

$$\Delta \underline{S}_{surr} = \int \frac{d\underline{Q}}{T_{surr}} = \frac{\underline{Q}}{300} = \frac{-4014}{300} = -13.38 \text{J/K}.$$ This is equal and opposite to the entropy

change of the piston/cylinder, so the overall entropy change is $\Delta S_{universe} = 0$.

For part 4.1(b), the entropy change of the universe is

$\Delta \underline{S}_{surr} = \underline{Q}/300 = -1995/300 = -6.65 \text{J/K}$. The total entropy change is

$\Delta S_{universe} = 13.38 - 6.65 = 6.73 \text{J/K} > 0$, thus entropy is generated when work is lost.

(b) If the temperature of the surroundings is raised to 310K, then for the reversible piston cylinder expansion for 4.1(a), $\Delta \underline{S}_{surr} = -4014/310 = -12.948 \text{J/K}$, and

$\Delta S_{universe} = 13.38 - 12.95 = 0.43 \text{J/K} > 0$. This process now will have some 'lost work' due to the temperature difference at the boundary even though the piston/cylinder and work was frictionless without other losses. We will reexamine heat transfer in a gradient in a later example. For case 4.1(b), the entropy generation is still greater, indicating more lost work,

$\Delta \underline{S}_{surr} = -1995/310 = -6.43 \text{J/K}$, $\Delta S_{universe} = 13.38 - 6.43 = 6.95 \text{J/K} > 0$.

Example 4.1 Entropy change and "lost work" in a gas expansion

An isothermal ideal gas expansion produces maximum work if carried out reversibly and less work if friction or other losses are present. One way of generating "other losses" is if the force of the gas on the piston is not balanced with the opposing force during the expansion, as shown in part (b) below. Consider a piston/cylinder containing one mole of nitrogen at 5 bars and 300 K is expanded isothermally to 1 bar.

(a) Suppose that the expansion is reversible. How much work could be obtained and how much heat is transferred? What is the entropy change of the gas?

(b) Suppose the isothermal expansion is carried out irreversibly by removing a piston stop and expanding against the atmosphere at 1 bar. Suppose that heat transfer is provided to permit this to occur isothermally. How much work is done by the gas and how much heat is transferred? What is the entropy change of the gas? How much work is lost compared to a reversible isothermal process and what percent of the reversible work is obtained (the efficiency)?

Solution:

Basis: 1 mole, closed unsteady-state system.

(a) The energy balance for the piston/cylinder is $\Delta U = Q + W_{EC} = 0$ because the gas is isothermal and ideal. $dW_{EC} = -PdV = -(nRT/V)dV$; $W_{EC} = -nRT\ln(V_2/V_1) = -nRT\ln(P_1/P_2) = -(1)8.314(300)\ln(5) = -4014J$. By the energy balance $Q = 4014J$.

The entropy change is by Eqn. 4.7, $\Delta S = -nR\ln(P_2/P_1) = -(1)8.314\ln(1/5) = 13.38$ J/K.

(b) The energy balance does not depend on whether the work is reversible and is the same.

Taking the atmosphere as the system, the work is $W_{EC,atm} = -P_{atm}(V_{2,atm} - V_{1,atm}) = -W_{EC} = -P_{atm}(V_1 - V_2) = P_{atm}(nRT/P_2 - nRT/P_1) = nRT(P_{atm}/P_2 - P_{atm}/P_1) =>$
$W_{EC} = nRT(P_{atm}/P_1 - P_{atm}/P_2) = (1)8.314(300)(1/5 - 1) = -1995J$, $Q = 1995J$.

The entropy change depends on only the state change and this is the same as (a), 13.38 J/K.

The amount of lost work is $W_{lost} = 4014 - 1995 = 2019J$, the percent of reversible work obtained (efficiency) is $1995/4014 \cdot 100\% = 49.7\%$.

Example 4.8 Entropy generation in a temperature gradient

A 500 mL glass of chilled water at 283 K is removed from a refrigerator. It slowly equilibrates to room temperature at 298 K. The process occurs at 1 bar. Calculate the entropy change of the water, ΔS_{water}, the entropy change of the surroundings, ΔS_{surr}, and the entropy change of the universe, ΔS_{univ}. Neglect the heat capacity of the container. For liquid water $C_P = 4.184$ J/g-K.

Solution:

Water: The system is closed at constant pressure with $T^i = 283$ K and $T^f = 298$ K. We choose any reversible pathway along which to evaluate Eqn. 4.13, a convenient path being constant-pressure heating. Thus,

$$dQ_{rev} = d\underline{H} = mC_P dT$$

$$\Delta \underline{S}_{water} = \int_{T^i}^{T^f} \frac{mC_P dT}{T_{sys}} = mC_P \ln\left(\frac{T^f}{T^i}\right) = 500(4.184)\ln\left(\frac{298}{283}\right) = 108.0\frac{J}{K} \qquad (*)$$

Surroundings: The surroundings also undergo a constant pressure process as a closed system; however, the heat transfer from the glass causes no change in temperature—the surroundings act as a reservoir and the temperature is 298 K throughout the process. The heat transfer of the surroundings is the negative of the heat transfer of the water, so we have

$$\Delta S_{surr} = \int_{T^i}^{T^f} \frac{dQ_{rev}}{T_{surr}} = -\int_{T^i}^{T^f} \frac{dQ_{rev, water}}{T_{surr}} = \frac{-mC_P \Delta T_{water}}{T_{surr}} = \frac{-31380J}{298K} = -105.3\frac{J}{K} \qquad (*)$$

Note that the temperature of the surroundings was constant, which simplified the integration.

Universe: For the universe we sum the entropy changes of the two subsystems that we have defined. Summing the entropy change for the water and the surroundings we have

$$\Delta \underline{S}_{univ} = 2.7\frac{J}{K}$$

Entropy has been generated. The process is irreversible.

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4.4 THE ENTROPY BALANCE

$$\frac{d\underline{S}}{dt} = \sum_{inlets} S^{in}\dot{m}^{in} - \sum_{outlets} S^{out}\dot{m}^{out} + \sum_{surfaces} \frac{\dot{\underline{Q}}}{T_{sys}} + \dot{\underline{S}}_{gen}$$

4.32

$$0 = \dot{m}(S^{in} - S^{out}) + \frac{\dot{\underline{Q}}}{T} + \dot{\underline{S}}_{gen}$$

4.33

$$d\underline{S} = \frac{d\underline{Q}}{T} + d\underline{S}_{gen}$$

4.34

Note: As we work examples for irreversible processes, *note that we do not apply the entropy balance to find entropy changes. We always calculate entropy changes by alternative reversible pathways that reach the same states, then we apply the entropy balance to find how much entropy was generated.*
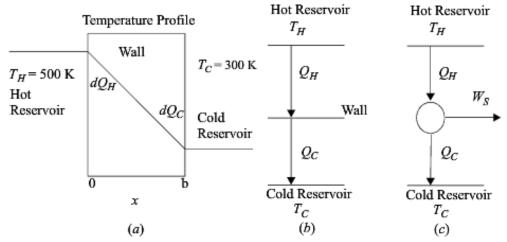
Alternatively, for reversible processes, *we do apply the entropy balance because we set the entropy generation term to zero.*

Example 4.9 Entropy balances for steady-state composite systems

Imagine heat transfer occurring between two reservoirs.

(a) A steady-state temperature profile for such a system is illustrated in Fig. (a) below. (Note that the process is an unsteady state with respect to the reservoirs, but the focus of the analysis here is on the wall.) The entire temperature gradient occurs within the wall. In this ideal case, there is no temperature gradient within either reservoir (therefore, the reservoirs are not a source of entropy generation). Note that the wall is at steady state. Derive the relevant energy and entropy balances, carefully analyzing three subsystems: the hot reservoir, the cold reservoir, and the wall. Note that a superficial view of the reservoirs and wall is shown in Fig. (b).

(b) Suppose the wall was replaced by a reversible Carnot engine across the same reservoirs, as illustrated in Fig. (c). Combine the energy and entropy balances to obtain the thermal efficiency.

(a) (b) (c)

Note: Keeping track of signs and variables can be confusing when the universe is divided into multiple subsystems. Heat flow on the hot side of the wall will be negative for the hot reservoir, but positive for the wall. Since the focus of the problem is on the wall or the engine, we will write all symbols from the perspective of the wall or engine and relate to the reservoirs using negative signs and subscripts.

Solution:

(a) Since the wall is at steady state, the energy balance for the wall shows that the heat flows in and out are equal and opposite:

$$0 = \sum_{boundaries} \dot{Q} = \dot{Q}_H + \dot{Q}_C \Rightarrow \dot{Q}_H = -\dot{Q}_C \qquad 4.35$$

The entropy balance in each reservoir simplifies:

$$\frac{dS_{H \text{ or } C}}{dt} = \sum_{in} S^{in} \dot{m}^{in} - \sum_{out} S^{out} \dot{m}^{out} + \frac{\dot{Q}}{T_{sys}} + \dot{S}_{gen}$$

The entropy generation term drops out because there is no temperature gradient in the reservoirs. Taking the hot reservoir as the subsystem and noting that we have defined Q_H and Q_C to be based on the wall, we write:

$$\frac{dS_H}{dt} = \frac{\dot{Q}}{T_H} = \frac{-\dot{Q}_{H,wall}}{T_H} \; ; \; \frac{dS_C}{dt} = \frac{\dot{Q}}{T_C} = \frac{-\dot{Q}_{C,wall}}{T_C} = \frac{\dot{Q}_{H,wall}}{T_C} \qquad 4.36$$

where the heat fluxes are equated by the energy balance.

Now consider the entropy balance for the wall subsystem. Entropy is a state property, and since no state properties throughout the wall are changing with time, entropy of the wall is constant, and the left-hand side of the entropy balance is equal to zero. Note that the entropy generation term is kept because we know there is a temperature gradient:

$$\frac{dS_{wall}}{dt} = 0 = \frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_C}{T_C} + \dot{S}_{gen, W}$$

Noting the relation between the heat flows in Eqn. 4.35, we may then write for the wall:

$$\dot{S}_{gen,wall} = \dot{Q}_H \left(\frac{1}{T_C} - \frac{1}{T_H} \right) \qquad 4.37$$

Then the wall with the temperature gradient is a source of entropy generation. Summarizing,

$$\frac{dS_{univ}}{dt} = \frac{dS_H}{dt} + \frac{dS_{wall}}{dt} + \frac{dS_C}{dt} = \frac{-\dot{Q}_{H,wall}}{T_H} + \frac{-\dot{Q}_{C,wall}}{T_C} = \dot{S}_{gen,wall} \qquad 4.38$$

Hence we see that the wall is the source of entropy generation of the universe, which is positive. Notice that inclusion of the wall is important in accounting for the entropy generation by the entropy balance equations.

(b) The overall energy balance relative for the engine is:

$$0 = \sum_{boundaries} \dot{Q} + \dot{W} = \dot{Q}_H + \dot{Q}_C + \dot{W}_S \Rightarrow \eta_\theta = \frac{-\dot{W}_S}{\dot{Q}_H} = \left(1 + \frac{\dot{Q}_C}{\dot{Q}_H} \right) \qquad 4.39$$

Example 4.9 Entropy balances for steady-state composite systems (Continued)

The the engine operates a steady-state cycle, $dS_{engine}/dt = 0$ (it is internally reversible):

$$0 = \sum_{in} S^{in} \dot{m}^{in} - \sum_{out} S^{out} \dot{m}^{out} + \sum_{boundaries} \frac{\dot{Q}}{T} + \dot{S}_{gen} = \frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_C}{T_C} \Rightarrow \frac{\dot{Q}_C}{\dot{Q}_H} = \frac{-T_C}{T_H} \qquad 4.40$$

As before, $\eta_\theta = -\dot{W}_S/\dot{Q}_H = (1 - T_C/T_H)$ and we have derived it using the entropy balance. Note that the heat flows are no longer equal and are such that the entropy changes of the reservoirs sum to zero.

$$\dot{W}_{S,net} = \dot{Q}_H \left(1 - \frac{T_C}{T_H}\right) = T_C \cdot \dot{Q}_H \left(\frac{1}{T_C} - \frac{1}{T_H}\right) \qquad 4.41$$

$$\dot{W}_{lost} = T_C \dot{S}_{gen} \qquad 4.42$$

T_C can be called the temperature at which the work is lost.

An entirely analogous analysis of heat transfer would apply if we ran the heat engine in reverse, as a heat pump. Only the signs would change on the direction the heat and work were flowing relative to the heat pump. Therefore, the use of entropy permits us to reiterate the Carnot formulas in the context of all fluids, not just ideal gases.

Carnot thermal efficiency.

$$\eta_\theta = \frac{-\dot{W}_{S,net}}{\dot{Q}_H} = \left(1 + \frac{\dot{Q}_C}{\dot{Q}_H}\right) = \left(1 - \frac{T_C}{T_H}\right) \text{, Carnot heat engine} \qquad 4.43$$

Carnot coefficient of performance.

$$COP \equiv \frac{\dot{Q}_C}{\dot{W}_{S,net}} = \left(\frac{T_H}{T_C} - 1\right)^{-1} = \frac{T_C}{T_H - T_C} \text{, Carnot refrigerator} \qquad 4.44$$

4.5 INTERNAL REVERSIBILITY

A *process* may be irreversible due to interactions at the boundaries (such as discussed in Example 4.9 on page 155) even when each system in the process is reversible. Such a process is called **internally reversible.** Such a *system* has no entropy generation *inside* the system boundaries. We have

(a) Heat engine   (b) Heat pump

Figure 4.5 *Schematic of a heat engine (a) and heat pump (b). The temperatures of the reservoirs are not required to match the reversible engine temperatures, but work is optimized if they do, as discussed in the text.*

Heat Engine

A schematic for a Carnot engine is shown in Fig 4.5(a). Heat is being transferred from the reservoir at T_2 to the reservoir at T_1, and work is being obtained as a result. In order for heat transfer to occur between the reservoirs and the heat engine in the desired direction, we must satisfy $T_2 \geq T_H > T_C \geq T_1$, and since the thermal efficiency is given by Eqn. 3.6, for maximum efficiency (maximum work), T_C should be as low as possible and T_H as high as possible, i.e., set $T_H = T_2$, $T_C = T_1$.

Heat Pump

A schematic for a Carnot heat pump is shown in Fig. 4.5(b). Heat is being transferred from a reservoir at T_1 to the reservoir at T_2, and work is being supplied to achieve the transfer. In order for heat transfer to occur between the reservoirs and the heat engine in the desired direction, we must satisfy $T_2 \leq T_H > T_C \leq T_1$. Since the COP is given by Eqn. 4.44, for maximum COP (minimum work), T_C should be as high as possible and T_H as low as possible, i.e., set $T_C = T_1$, $T_H = T_2$ *Therefore, optimum work interactions occur when the Carnot device operating temperatures match the surrounding temperatures.* We use this feature in future calculations without special notice.

4.6 ENTROPY BALANCES FOR PROCESS EQUIPMENT

Simple Closed Systems

Example 4.10 Entropy generation by quenching

A carbon-steel engine casting [$C_P = 0.5$ kJ/kg°C] weighing 100 kg and having a temperature of 700 K is heat-treated to control hardness by quenching in 300 kg of oil [$C_P = 2.5$ kJ/kg°C] initially at 298 K. If there are no heat losses from the system, what is the change in entropy of: (a) the casting; (b) the oil; (c) both considered together; and (d) is this process reversible?

Solution: Unlike the previous examples, there are no reservoirs, and the casting and oil will both change temperature. The final temperature of the oil and the steel casting is found by an energy balance. Let T^f be the final temperature in K.

Energy balance: The total change in energy of the oil and steel is zero.
Heat lost by casting:
$$Q = mCp\Delta T = 100\,(0.5)\,(700 - T^f)$$
Heat gained by oil:
$$Q = mCp\Delta T = 300\,(2.5)\,(T^f - 298) \Rightarrow \text{balancing the heat flow, } T^f = 323.1 \text{ K}$$

Entropy balance: The entropy change of the universe will be the sum of the entropy changes of the oil and casting. We will not use the entropy balance directly except to note that $\Delta \underline{S}_{univ} = \underline{S}_{gen}$. We can calculate the change of entropy of the casting and oil by any reversible pathway which begins and ends at the same states. Consider an isobaric path:

$$\text{Using the macroscopic definition} \Rightarrow \quad \Delta \underline{S} = \int \frac{dQ}{T} = m\int \frac{C_P}{T}\,dT = mC_P\,\ln\!\left(\frac{T_2}{T_1}\right) \qquad (*)$$

(a) Change in entropy of the casting:

$$\Delta \underline{S} = 100\,(0.5)\,\ln[323.1/700] = -38.7 \text{ kJ/K} \qquad (*)$$

(b) Change in entropy of the oil (the oil bath is of finite size and will change temperature as heat is transferred to it):

$$\Delta \underline{S} = 300\,(2.5)\,\ln[323.1/298] = 60.65 \text{ kJ/K} \qquad (*)$$

(c) Total entropy change: $\underline{S}_{gen} = \Delta \underline{S}_{univ} = 60.65 - 38.7 = 21.9$ kJ/K
(d) $\underline{S}_{gen} > 0$; therefore irreversible; compare the principles with Example 4.8 on page 152 to note the similarities. The difference is that both subsystems changed temperature.

Heat Exchangers

The entropy balance for a standard two-stream heat exchanger is given by Eqn. 4.45. Since the unit is at steady state, the left-hand side is zero. Applying the entropy balance around the *entire* heat exchanger, there is no heat transfer *across* the system boundaries (in the absence of heat loss), so the heat-transfer term is eliminated. Since heat exchangers operate by conducting heat across tubing walls with finite temperature driving forces, we would expect the devices to be irreversible. Indeed, if the inlet and outlet states are known, the flow terms may be evaluated, thus permitting calculation of entropy generation.

$$\cancel{\frac{dS}{dt}} = \sum_{in} S^{in} \dot{m}^{in} - \sum_{out} S^{out} \dot{m}^{out} + \cancel{\frac{\dot{Q}}{T_{sys}}} + \dot{S}_{gen} \qquad \text{4.45}$$
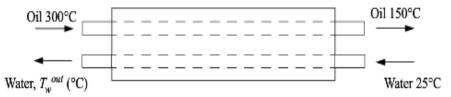
We also may perform "paper" design of ideal heat transfer devices that operate reversibly. If we set the entropy generation term equal to zero, we find that the inlet and outlet states are constrained. Since there are multiple streams, the temperature changes of the streams are coupled to satisfy the entropy balance. In order to construct such a reversible heat transfer device, the unit would need to be impracticably large to only have small temperature gradients.

Example 4.11 Entropy in a heat exchanger

A heat exchanger for cooling a hot hydrocarbon liquid uses 10 kg/min of cooling H_2O which enters the exchanger at 25°C. Five kg/min of hot oil enters at 300°C and leaves at 150°C and has an average specific heat of 2.51 kJ/kg-K.

(a) Demonstrate that the process is irreversible as it operates now.

(b) Assuming no heat losses from the unit, calculate the maximum work which could be obtained if we replaced the heat exchanger with a Carnot device which eliminates the water stream and transfers heat to the surroundings at 25°C

Oil 300°C → → Oil 150°C
Water, T_w^{out} (°C) ← ← Water 25°C

Solution:

(a) System is heat exchanger (open system in steady-state flow)
Energy balance:

$$\Delta H_{oil}\dot{m}_{oil} + \Delta H_{water}\dot{m}_{water} = 0$$

$$10(4.184)(T_w^{out} - 25) + 5(2.51)(150 - 300) = 0; \quad T_w^{out} = 70°C$$

Entropy balance:

$$\Delta S_{oil}\dot{m}_{oil} + \Delta S_{water}\dot{m}_{water} = \dot{S}_{gen}$$

$$dS_i = dQ/T = C_P\, dT/T \Rightarrow \Delta S_i = C_{Pi}\ln(T_i^{out}/T_i^{in}) \quad (*)$$
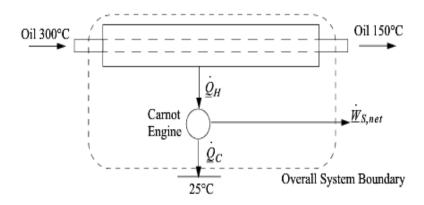
$$\Delta S_{oil} = C_P\ln(T^{out}/T^{in}) = (2.51)\ln(423.15/573.15) = -0.7616 \text{ kJ/kgK} \quad (*)$$

$$\Delta S_{water} = C_P\ln(T^{out}/T^{in}) = (4.184)\ln(343.15/298.15) = 0.5881 \text{ kJ/kgK} \quad (*)$$

$$\dot{S}_{gen} = \Delta S_{oil}\dot{m}_{oil} + \Delta S_{water}\dot{m}_{water} = 5(-0.7616) + 10(0.5881) = 2.073 \text{ kJ/K-min}$$

The process is irreversible because entropy is generated.

(b) The modified process is represented by the "device" shown below. Note that we avoid calling the device a "heat exchanger" to avoid confusion with the conventional heat exchanger. To simplify analysis, the overall system boundary is used.

Oil 300°C → → Oil 150°C
$\dot{Q}_H$
Carnot Engine → $\dot{W}_{S,net}$
$\dot{Q}_C$
25°C — Overall System Boundary

By an energy balance around the overall system, $0 = \dot{n}(H^{in} - H^{out}) + \dot{Q}_C + \dot{W}_S$. We can only solve for the enthalpy term,

$$\dot{m}(H^{in} - H^{out}) = \dot{m}C_p(T^{in} - T^{out}) = 5(2.51)(300 - 150) = 1882.5 \text{ kJ/min}$$

Since heat and work are both unknown, we need another equation. Consider the entropy balance, which, since it is a reversible process, $\dot{S}_{gen} = 0$, gives

$$0 = \dot{m}(S^{in} - S^{out}) + \frac{\dot{Q}_C}{T}, \qquad \dot{Q}_C = 298.15 \cdot (-0.7616) \cdot 5 = -1135 \text{ kJ/min}$$

Now inserting these results into the overall energy balance gives the work,

$$\dot{W}_S^{net} = -1883. + 1135. = -748 \text{ kJ/min}$$

Throttle Valves

Steady-state throttle valves are typically assumed to be adiabatic, but a finite pressure drop with zero recovery of work or kinetic energy indicates that $\dot{S}_{gen} > 0$. Throttles are isenthalpic, and for an ideal gas, they are thus isothermal, $\Delta S^{ig} = C_P \ln(T/T^i) - R\ln(P^{out}/P^{in})$. For a real fluid, temperature changes can be significant. The entropy increase is large for gases, and small, but non-zero for liquids. It is important to recall that liquid streams near saturation may flash as they pass through throttle valves, which also produces large entropy changes and significant cooling of the process fluid even when the process is isenthalpic. Throttles involving flash are common in the liquefaction and refrigeration processes discussed in the next chapter. Throttles are always irreversible.

Nozzles

Steady-state nozzles can be designed to operate nearly reversibly; therefore, we may assume $\underline{S}_{gen} = 0$, and Eqn. 4.47 applies. Under these conditions, thrust is maximized as enthalpy is converted into kinetic energy. The distinction between a nozzle and a throttle is based on the reversibility of the expansion. Recall from Chapter 2 that a nozzle is specially designed with a special taper to avoid turbulence and irreversibilities. Naturally, any real nozzle will approximate a reversible one and a poorly designed nozzle may operate more like a throttle. Proper design of nozzles is a matter of fluid mechanics. We can illustrate the basic thermodynamic concepts of a properly designed nozzle with an example.

Example 4.12 Isentropic expansion in a nozzle

Steam at 1000°C and 1.1 bars passes through a horizontal adiabatic converging nozzle, dropping to 1 bar. Estimate the temperature, velocity, and kinetic energy of the steam at the outlet assuming the nozzle is reversible and the steam can be modeled with the ideal gas law under the conditions. Consider the initial velocity to be negligible. The highest exit velocity possible in a converging nozzle is the speed of sound. Use the NIST web site[a] as a resource for the speed of sound in steam at the exit conditions.

Solution:

Energy balance: $\Delta H = -m\Delta v^2/2$ Entropy balance (reversible): $\Delta S = 0$.

For an isentropic reversible expansion the temperature will drop. We will approximate the heat capacity with an average value. Let us initially use a C_P for 650 K. Estimating the heat capacity from Appendix E at 650 K, the polynomial gives $C_P = 44.6$ J/mol, $R/C_P \sim 8.314/44.6 = 0.186$. The following relation satisfies the entropy balance for an adiabatic, reversible, ideal gas (Eqn. 4.29):

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{R/C_P} = (1.1)^{-0.186} = 0.9824 \Rightarrow T_2 = 1273(0.9824) = 1250.5 \text{ K} \qquad (*)$$

The temperature change is small, so the constant heat capacity assumption is fine. The enthalpy change is $-\Delta H = -C_P\Delta T = 44.6(1273 - 1250.5)(\text{J/mol}) = 1004$ J/mol.

Assuming that the inlet velocity is low, $v_1 \sim 0$ and converting the enthalpy change to the change in velocity gives $v^2 = -2\Delta H/m = 2 \cdot 1004\text{J/mol}(\text{mol}/18.01\text{g})(1000\text{g/kg})(1\text{kg-m}^2/\text{s}^2)/\text{J} = 111,500$ m²/s², or $v = 334$ m/s. According to the NIST web site at 1250K and 0.1MPa, the speed of sound is 843 m/s. The design is reasonable.

Adiabatic Turbine, Compressor, and Pump

The entropy balance for a steady-state *adiabatic* device is:

$$\cancel{\frac{dS}{dt}} = \sum_{in} S^{in} \dot{m}^{in} - \sum_{out} S^{out} \dot{m}^{out} + \cancel{\frac{\dot{Q}}{T_{sys}}} + \dot{S}_{gen} \qquad 4.46$$

The left-hand side drops out because the system is at steady state. If the device is reversible, $\dot{S}_{gen}$ is zero. Further, these devices typically have a single inlet or outlet,[17] and $\dot{m}^{in} = \dot{m}^{out}$, thus,

$$S^{out'} = S^{in'} \qquad 4.47$$

❶ Adiabatic reversible turbine, compressor, and pump.

Therefore, if we know the inlet state, we can find S^{in}. The outlet pressure is generally given, so for a pure fluid, the outlet state is completely specified by the two state variables S^{out} and P^{out}. We

4.7   TURBINE, COMPRESSOR, AND PUMP EFFICIENCY

❶ Primes are used to denote reversible processes.

$$\text{pump or compressor efficiency} = \boxed{\eta_C = \frac{W'}{\underline{W}} \times 100\%} \qquad 4.48$$

$$\text{turbine or expander efficiency} = \boxed{\eta_E = \frac{W}{W'} \times 100\%} \qquad 4.49$$

Summary of Process and General Rules

Nozzle $\Delta S = 0$

$\Delta H = \Delta(1/2\ mv^2)$

Throttle $\Delta S = -R\ln(P_2/P_1)$ (i.g.)

$\Delta H = 1/2\ mv^2$

Generally $\Delta H = 0$

Pump $\Delta S = 0$ for adiabatic reversible

$\Delta H = W_S = \Delta H' / \eta_{eff}$

Turbine $\Delta S = 0$ for adiabatic reversible

$\Delta H = W_S = \Delta H'\ \eta_{eff}$

Carnot (Use °K)

Engine $\eta_{eff} = (T_H - T_C)/T_H$

Refrigerator $COP = T_C/(T_H - T_C)$

Heat Pump $COP = T_H/(T_H - T_C)$

Isothermal $(\Delta S)_T = R\ \ln[V_2/V_1]$ i.g.

$= -R\ \ln[P_2/P_1]$

$(\Delta H)_T = 0$

Ideal Mixing $\Delta S_{mix} = -R\ \Sigma x_i\ \ln x_i$

Adiabatic, Reversible

$\Delta S = 0$

Isobaric $(dS)_P = C_p\ (dT)_P/T$

$(dS/dT)_P = C_p/T$

Constant Volume

$(dS)_V = C_V\ (dT)_V/T$

$(dS/dT)_V = C_V/T$

Phase Change $\Delta S_{trans} = \Delta H_{trans}/T_{trans}$

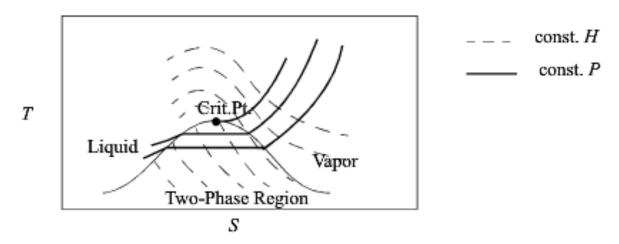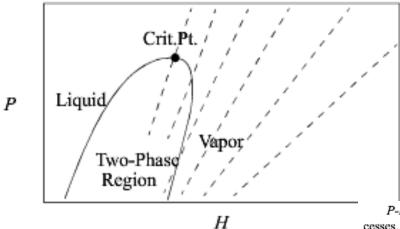## 4.8 VISUALIZING ENERGY AND ENTROPY CHANGES

Figure 4.6 *Illustration of a T-S diagram showing lines of constant pressure and enthalpy.*

Turbines, compressors, and pumps occur so frequently that we need convenient tools to aid in process calculations. Visualization of the state change is possible by plotting entropy on charts. This technique also permits the charts to be used directly in the process calculations. One common representation is the T-S chart shown in Fig. 4.6. The phase envelope appears as a fairly symmetrical hump. A reversible turbine, compressor, or pump creates state changes along a vertical line on these coordinates. Lines of constant enthalpy and pressure are also shown on these diagrams, as sketched in the figure. Volumes are also usually plotted, but they lie so close to the pressure lines that they are not illustrated in the figure here to ensure clarity.
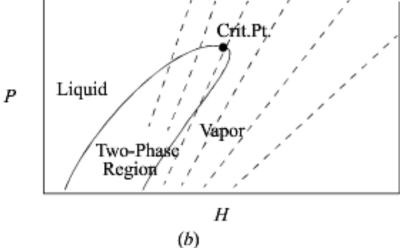
Visualizing state changes on charts will be helpful when using tables or computers for physical properties.

(a)

P-H diagrams shown in Fig. 4.7 are also useful; they are used frequently for refrigeration processes. The phase envelope tends to lean to the right because the enthalpies of vapor and liquid are both increasing along the saturation curve until the critical point is approached, where the vapor-phase enthalpy decreases due to significant non-idealities. Lines of constant entropy on these plots are slightly diagonal with a positive slope as shown in Fig. 4.7(a). For some hydrocarbons and halogenated compounds, the phase envelope can lean more sharply than the isentropic lines as shown in Fig. 4.7(b). A reversible compressor will operate along a line of constant entropy.

(b)

- - - -   const. *S*

Figure 4.7 *Illustration of a P-H diagram showing (a) lines of constant entropy for a species where the saturation curve leans less than isentropes (e.g., water) and (b) illustration of a P-H diagram showing lines of constant entropy for a species where the saturation curve leans more than isentropes (e.g., hexane).*
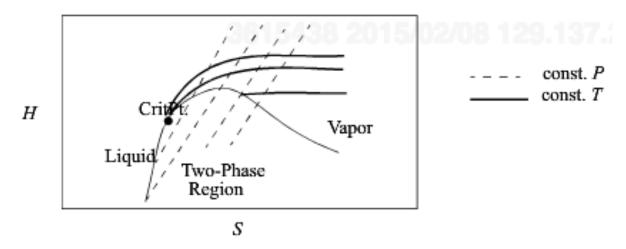
Figure 4.8 *Illustration of an H-S (Mollier) diagram showing lines of constant entropy.*

Another convenient representation of entropy is the *H-S* diagram (Mollier diagram). In this diagram, lines of constant pressure are diagonal, and isotherms have a downward curvature as in Fig. 4.8. The saturation curve is quite skewed.

Determining Turbine Outlet Conditions

(i) Reversible outlet one phase, actual outlet one phase;

(ii) Reversible outlet two phase, actual outlet one phase;

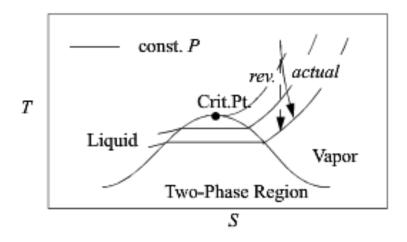(iii) Reversible outlet two phase, actual outlet two phase.

Figure 4.9 *Illustration of a reversible and actual (irreversible) turbine on a T-S diagram.*
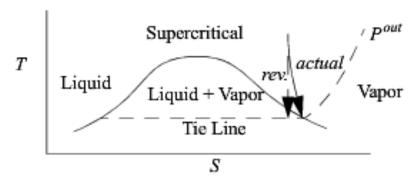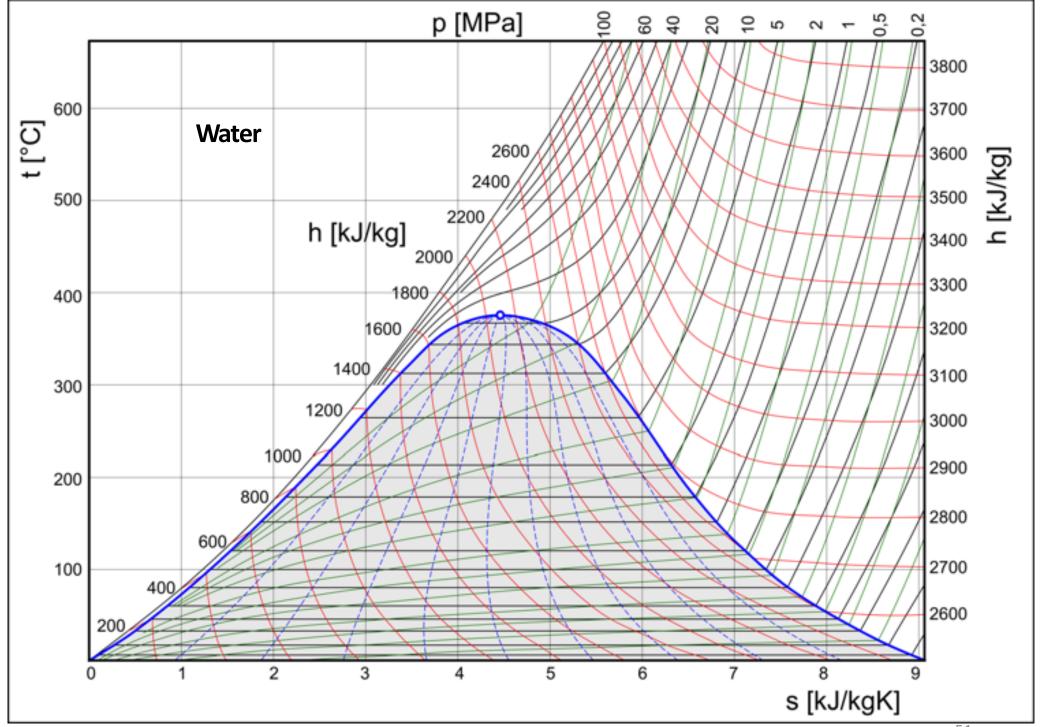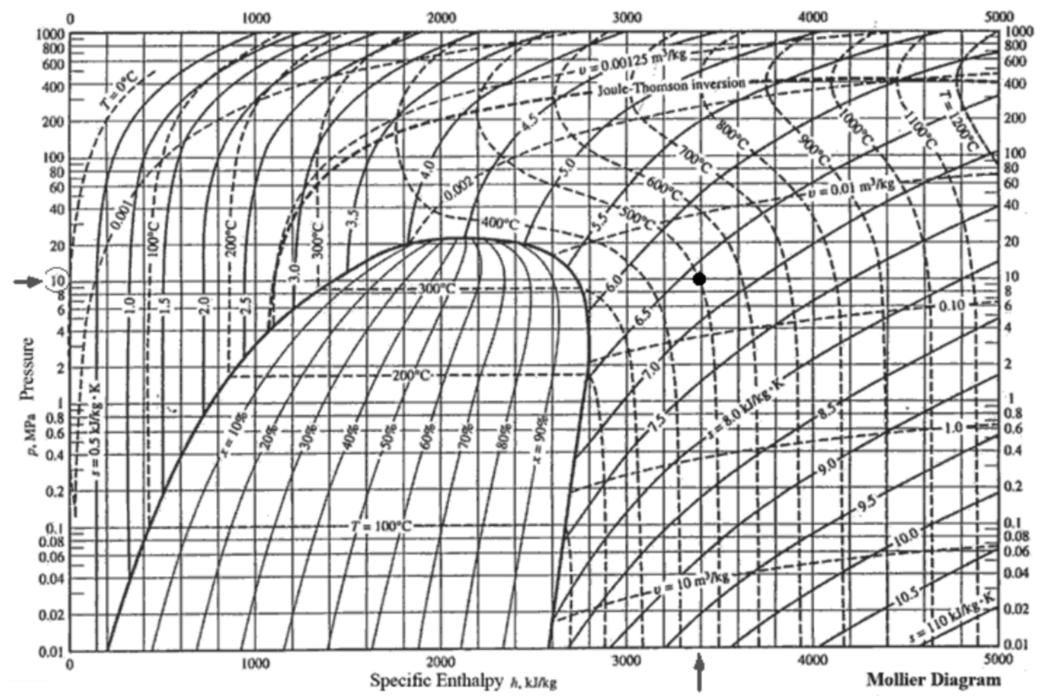

Figure 4.10 *Illustration of need for quality calculation on turbine outlet where the actual outlet is saturated steam.*

in Fig. 4.9 where the outlets for the reversible and irreversible cases are both one phase. Since the reversible adiabatic turbine is isentropic, the line representing the reversible process must be vertical. As shown in Fig. 4.10, if the upstream entropy is less than the saturated vapor entropy at the outlet pressure, the *reversible* outlet ends up *inside the liquid-vapor region*, to the left of the saturated vapor curve. In this case, we must perform a quality calculation to determine the vapor fraction. Since the actual turbine must have an outlet state of higher entropy, due to entropy generation, the outlet state can lie inside the phase envelope, on the saturation curve, or outside the phase envelope, depending on the proximity of the reversible outlet state to the saturation curve and also depending on the turbine efficiency. A frequent question is, "How do I know when I need a quality calculation?" The calculation is required if the *inlet* entropy is less than the saturation entropy at the

Water

Mollier Diagram

Specific Enthalpy h, kJ/kg

p, MPa   Pressure

Mollier-h, s Diagram

for Water Steam

Enthalpy h in kJ/kg

Entropy s in kJ/(kg x K)

p=1000 bar
p=600 bar
0.01 m3/kg
0.02 m3/kg
p=100 bar
0.1 m3/kg
0.2 m3/kg
p=10 bar
1.0 m3/kg
2.0 m3/kg
p=1 bar
10.0 m3/kg
20.0 m3/kg
p=0.1 bar
100.0 m3/kg
p=0.01 bar

t=800 C
t=700 C
t=600 C
t=500 C
t=400 C
t=300 C
t=200 C
t=100 C

x = 100%
x = 90%
x = 80%
x = 70%
x = 60%
x = 50%
x = 40%
x = 30%
x = 20%
x = 10%
x = 0%

Critical point
T=647.3K
p=221.2bar
v=0.00317 m3/kg

T=573K
T=523K T=473K
T=423K
T=373K
T=323K
T=623K

T=623K
T=573K
T=523K
T=473K
T=423K
T=373K
T=323K
T=273K

Example 4.13 Various cases of turbine outlet conditions

An adiabatic turbine inlet (state 1) is 500°C and 1.4 MPa. For each of the following outlet conditions (state 2), determine the specified quantities.

(a) $P_2 = 0.6$ MPa, $\eta_E = 0.85$. Find W_S, H_2, S_2, and T_2.
(b) $P_2 = 0.03$ MPa, $\eta_E = 0.85$. Find W_S, H_2, S_2, and T_2.
(c) $P_2 = 0.01$ MPa, $\eta_E = 0.9$. Find W_S, H_2, S_2, and T_2.

Note that using a common inlet state for each of the cases will permit us to skip the steps to determine the inlet state as we work the different alternatives.

Solution: First, the inlet properties are determined: $H_1 = 3474.8$ kJ/kg, $S_1 = 7.6047$ kJ/kg-K. The reversible calculation is performed for each outlet condition, recognizing that a reversible turbine is isentropic.

(a) $S_2' = S_1 = 7.6047$ kJ/kg-K. Comparing with $S^{satV} = 6.7593$ kJ/kg-K at $P_2 = 0.6$ MPa, $S_2' > S^{satV}$, **so the reversible outlet state is superheated and any irreversibility must lead to greater entropy and greater superheat (case (i)).** This is the case of Fig. 4.9. Interpolating:

T (°C)	H (kJ/kg)	S (kJ/kg-K)
350	3166.1	7.5481
		7.6047
400	3270.8	7.7097

$$H_2' = 3166.1 + \frac{7.6047 - 7.5481}{7.7097 - 7.5481}(3270.8 - 3166.1) = 3202.8 \text{ kJ/kg}$$

By similar interpolation, $T_2' = 367.5$°C.

$$\Delta H = W_S' = 3202.8 - 3474.8 = -272.0 \text{ kJ/kg}$$

Applying η_E calculation, $\Delta H = W_S = \eta_E \Delta H = 0.85(-272) = -231.2$ kJ/kg,

$$H_2 = H_1 + \Delta H = 3474.8 - 231.2 = 3243.6 \text{ kJ/kg}$$

Preparing for interpolation:

T (°C)	H (kJ/kg)	S (kJ/kg-K)
350	3166.1	7.5481
	3243.6	
400	3270.8	7.7097

$$S_2 = 7.5481 + \frac{3243.6 - 3166.1}{3270.8 - 3166.1}(7.7097 - 7.5481) = 7.6677 \text{ kJ/kg-K}$$

By similar interpolation, $T_2 = 387.0$°C. We see that irreversibility has warmed the outlet, but not "heated" it, because it was adiabatic. With a one-phase outlet, $T_2 > T_2'$ if $\eta_E < 1$.

(b) The pressure is lower than part (a), and the saturated vapor S will be larger, and near the saturation boundary.

Recall that $S_2' = S_1 = 7.6047$ kJ/kg-K. Comparing with $S^{satV} = 7.7675$ kJ/kg-K at $P_2 = 0.03$ MPa, $S_2' < S^{satV}$, so the reversible outlet state is two-phase. This is the case of Fig. 4.10 and we need to proceed further to determine if the actual state is inside or outside the phase envelope. Interpolating using the saturation entropy values along with the S_2' at $T_2' = 69.1$°C,

$$q' = \frac{S - S^{satL}}{\Delta S^{vap}} = \frac{7.6047 - 0.9441}{6.8234} = 0.976$$

Using Eqn. 1.27:

$$H_2' = 289.27 + 0.976(2335.28) = 2568.5 \text{ kJ/kg}$$

$$\Delta H = W_S' = 2568.5 - 3474.8 = -906.3 \text{ kJ/kg}$$

Applying η_E calculation, $\Delta H = W_S = \eta_E \Delta H = 0.85(-906.3) = -770.35$ kJ/kg,

$$H_2 = H_1 + \Delta H = 3474.8 - 770.35 = 2704.4 \text{ kJ/kg}$$

Comparing H_2 with $H^{satV} = 2624.55$ kJ/kg at $P_2 = 0.03$ MPa, $H_2 > H^{satV}$, so the outlet state is superheated (outside the phase envelope). **This is an instance of case (ii).**

To conclude the calculations, a double interpolation is required. Performing the first interpolation between 0.01 and 0.05 MPa will bracket the outlet state. (Note: 0.03 MPa is halfway between 0.01 and 0.05 MPa, so tabulated values are obtained by averaging rather than by a slower interpolation.)

T (°C)	H (kJ/kg)	S (kJ/kg-K)
100	(2687.5 + 2682.4)/2 = 2684.95	(8.4489 + 7.6953)/2 = 8.0721
	2704.4	
150	(2783.0 + 2780.2)/2 = 2781.6	(8.6892 + 7.9413)/2 = 8.3153

Interpolating:

$$S_2 = 8.0721 + \frac{2704.4 - 2684.95}{2781.6 - 2684.95}(8.3153 - 8.0721) = 8.121 \text{ kJ/kg-K}$$

Similarly, by interpolation, $T_2 = 110.1$°C.

Note: The reversible state is two-phase, and the actual outlet is one-phase for part (b). Also, $S_2 > S_2' = S_1$ and $H_2 > H_2'$ which are always true for irreversible turbines. $T_2 > T_2'$, which is a general result for one-phase output.

(c) Very low-outlet pressures shifts the saturation value of S to even higher values, making it more likely that the outlet will be two phase, case (iii).

$S_2' = S_1 = 7.6047$ kJ/kg-K. Comparing with $S^{satV} = 8.1488$ kJ/kg-K at $P_2 = 0.01$ MPa, $S_2' < S^{satV}$, so the reversible outlet state is two-phase. This is the case of Fig. 4.10 and we need to proceed further to determine if the actual state is inside or outside the phase envelope. Interpolating at $P = 0.01$ MPa ($T_2' = 45.81$°C),

$$q' = \frac{7.6047 - 0.6492}{7.4996} = 0.9274$$

Using Eqn. 1.27,

$$H_2' = 191.81 + 0.9274(2392.05) = 2410.2 \text{ kJ/kg}$$

$$\Delta H' = W_S' = 2410.3 - 3474.8 = -1064.6 \text{ kJ/kg}$$

Applying η_E calculation, $\Delta H = W_S = \eta_E \Delta H' = 0.90(-1064.6) = -958.1$ kJ/kg,

$$H_2 = H_1 + \Delta H = 3474.8 - 958.1 = 2516.7 \text{ kJ/kg.}$$

Comparing H_2 with $H^{satV} = 2583.86$ kJ/kg at $P_2 = 0.01$ MPa, $H_2 < H^{satV}$, so **the actual outlet state is two-phase as well as the reversible outlet (case (iii))**. For the actual outlet, H_2 gives:

$$q = \frac{2516.7 - 191.81}{2392.05} = 0.972$$

Using Eqn. 1.27,

$$S_2 = 0.6492 + 0.972(7.4996) = 7.9388 \text{ kJ/kg}$$

The actual outlet is wet steam at $T_2 = 45.81°C$. The reversible outlet and the actual outlet are both wet steam for part (c). Also, $S_2 > S_2' = S_1$ and $H_2 > H_2'$ which are always true for irreversible turbines. For case (c), $T_2 = T_2'$, however $q_2 > q_2'$, a general result for a two-phase outlet.

Example 4.14 Turbine efficiency calculation

An adiabatic turbine inlet is at 500°C and 1.4 MPa. Its outlet is at 0.01MPa and $q = 99\%$.

(a) Compute the work of the turbine.
(b) Compute the work of a reversible turbine.
(c) Compute the efficiency of the turbine and the entropy generation of the actual turbine.

Solution: The energy balance is $\Delta H = W_S$.

(a) The inlet is the same as Example 4.13: $H_1 = 3474.8$; $S_1 = 7.6047$. At the outlet,

$$H_2 = 191.81 + 0.99(2392.05) = 2559.9 \ \text{kJ/kg}$$

$$\Delta H = W_S = 2559.9 - 3474.8 = -914.9 \ \text{kJ/kg}$$

(b) Entropy balance: $\Delta S' = 0 => S_2' = S_1 = 7.6047$ kJ/kg-K.
It is slightly ambiguous whether we should match the outlet pressure or the specification of quality. By convention, it is assumed that pressure is the desired criterion (or temperature in a similar situation) because this pertains to the physical constraints of the design. This means that the reversible work is the same as Example 4.13(c) and $W_S' = -1064.6$ kJ/kg.

(c) The turbine efficiency is defined by $\eta_E = W_S/W_S' = 914.9/1064.6 = 85.9\%$.
The entropy generation is given by $S_{gen} = S_2 - S_2'$.

$$S_2 = 0.6492 + 0.99(7.4996) = 8.0738 \ \text{kJ/kg-K}$$

Referring to the entropy balance, $S_2' = S_1 = 7.3046$ so $S_{gen} = 8.0738 - 7.6047 = 0.4691$ J/g-K.

Another type of calculation involves determining a turbine inlet that will result in a certain outlet. The procedure is to use the outlet state to estimate the inlet entropy as a crude guess, and then use trial and error inlet conditions until the desired outlet state is matched.

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Example 4.15 Turbine inlet calculation given efficiency and outlet

An adiabatic turbine outlet (state 2) is 99% quality steam at 0.01 MPa, $\eta_E = 85\%$. The inlet pressure has been specified as 0.6 MPa. An absolute pressure of 0.6 MPa is conventionally defined as low pressure steam and is often applied in chemical processing. Find W_S, H_1, S_1, and T_1.

Solution: "Coincidentally," the outlet properties were determined in Example 4.14:
$H_2 = 2559.9$; $S_2 = 8.0738$. Referring to the superheated steam tables at 0.6 MPa, we seek an entropy value that is less than 8.0738 kJ/kg-K because $\eta_E < 100\%$ means entropy is generated. This occurs around 500°C. Trying 500°C, gives $H_1 = 3483.4$ kJ/kg and $S_1 = 8.0041$ kJ/kg-K. Then $W_S = -923.5$ kJ/kg; $q' = (8.0041 - 0.6492)/7.4996 = 0.9807$;
So $H_1' = 191.8 + 0.9807(2392) = 2537.6$ kJ/kg; $W_S' = 2537.6 - 3483.4 = -945.8$ kJ/kg;
$W_{lost} = 945.8 - 923.5 = 22.3$ kJ/kg; $\eta_E = -923.5/(-923.5 - 22.3) = 97.7\%$.

Further trials generate the values tabulated below. The last temperature is estimated by interpolation. (Hint: It would be great practice for you to compute these and check your answers.).

T	H_1	S_1	W_S	W_{lost}	η_E
450	3376.5	7.8611	−816.6	67.9	92.3%
400	3270.8	7.7097	−710.9	116.2	86.0%
350	3166.1	7.5481	−606.2	167.8	78.3%
393.8	3257.7	7.6895	−697.8	122.6	85.0%

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Multistage Turbines

(a) Explicit representation of stages

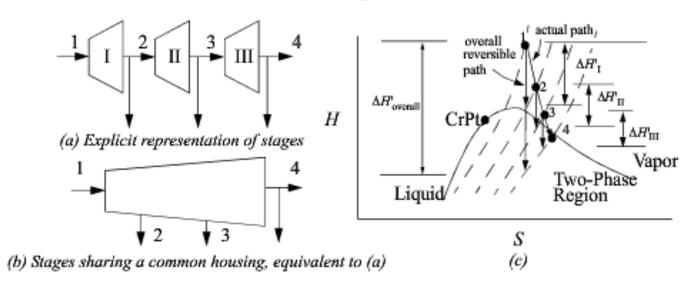(b) Stages sharing a common housing, equivalent to (a)

(c)

Figure 4.11 *Illustration that overall efficiency of an adiabatic turbine will be higher than the efficiency of the individual stages.*

slightly closer together at the bottom of the diagram than at the top. The overall efficiency is given by $\eta_E^{overall} = \dfrac{H_4 - H_1}{\Delta H'_{overall}}$, and the efficiency of an individual stage is given by

$\eta_{E,i} = \dfrac{H_{i+1} - H_i}{\Delta H'_i}$. If we consider the reversible work as $\Delta H'_{overall}$, that quantity must be smaller

than $\sum\limits_{stages} \Delta H'_i$. In fact, because the isobar spacing is increasing to the right of the diagram, the

vertical drop between any isobars on the line marked as the overall reversible path must be smaller than the vertical drop between the same two isobars starting along the actual path (except for the very first turbine). Therefore, the efficiency calculated for the overall system must be higher than the efficiency for the individual stages. This comparison does not imply that staging turbines alters their performance. The difference in efficiencies is due to differences in what is considered to be the basis for the reversible calculation. The cautionary note to retain from this discussion is that the distinction between overall or individual efficiencies is important when communicating the performance of a staged turbine system.

Overall turbine efficiency will be greater than stage efficiencies for the same total work output.
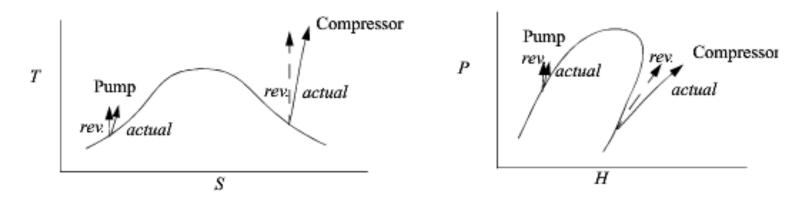
4.10 PUMPS AND COMPRESSORS

Figure 4.12 *Illustrations of pathways for reversible and irreversible pumps and compressors. The P-H diagram is for a system like Fig. 4.7(a).*

straightforward. Consider the case where the inlet state and the outlet pressure is known. First, the reversible outlet state is determined based on the isentropic condition, and the enthalpy at the reversible state is known. The most common estimate for compressors is described in Example 2.12 on page 76. Even though it is intended for ideal gases, it is convenient for many applications and often provides a reasonable first approximation. The most common estimate for pumps is described in Eqn. 2.32 on page 55. These both pertain to reversible processes. The efficiency can then be used to determine the actual outlet enthalpy and work, using Eqn. 4.46.

Example 4.16 Isothermal reversible compression of steam

In Example 2.12 on page 76, we mentioned that computing the work for isothermal compression of steam was different from computing the work for an ideal gas. Now that you know about the entropy balance, use it to compute the work of continuously, isothermally, and reversibly compressing steam from 5 bars and 224°C to 25 bars. Compare to the result of the ideal gas formula.

Solution: Energy balance: $\Delta H = Q + W$. Entropy balance: $\Delta S = Q/T$. Note that $\Delta S \neq 0$, even though this is a reversible process. $S_{gen} = 0$, but the process is not adiabatic. From the steam tables, we note that 224°C and 25 bars is practically equal to the saturated vapor. For the vapor at 224°C and 25 bars, interpolation gives $H = 2910.5$, $S = 7.1709$. Noting $Q = T\Delta S$,

$Q = (224 + 273.15)(6.2558 - 7.1709) = -454.94$; $W = (2801.9 - 2910.5) + 454.94 = 346.3$ J/g.

By the ideal gas formula, $W = 8.314(4.04)(224 + 273.15)\ln(5)/18 = 1493.1$ J/g.

The work is less for the real vapor because of the intermolecular attractions. The difference was particularly large in this case because the final pressure was fairly high (> 10 bars).
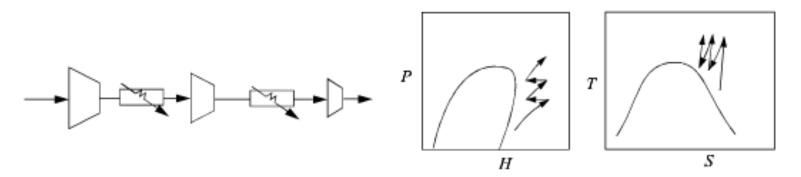
Multistage Compression

Figure 4.13 *Illustration of a multistage compression and the corresponding P-H diagram. On the P-H diagram, the compressors appear as the curves of increasing pressure and the heat exchangers are the horizontal lines at constant pressure.*
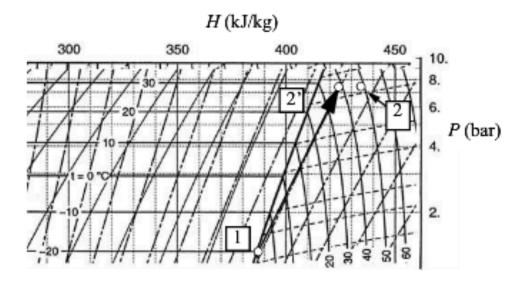
During adiabatic compression of vapors, the temperature rises. This can cause equipment problems if the temperature rise or pressure ratio (P^{out}/P^{in}) is too large. To address this problem, interstage cooling is used to lower the gas temperature between compression stages. Such operations are common when high pressures need to be reached. A schematic of a compressor with interstage cooling is shown in Fig. 4.13. The total work for multistage compression is generally given by summing the work of each stage using Eqn. 2.69 on page 77. However, the ideal gas law becomes less reliable as the stagewise inlet pressure increases. If the inlet pressure is above 10 bars and the reduced temperature is less than 1.5, nonideality effects should be evaluated. Methods to evaluate gas non-idealities and to calculate entropy for all manner of non-ideal gases are discussed in Unit II. For common refrigerants, it is convenient to apply charts that are functionally equivalent to the steam tables. The charts are difficult to read and precision is relatively low compared to using the steam tables. Example 4.17 illustrates the procedure using the refrigerant R134a.

Example 4.17 Compression of R134a using *P-H* chart

A compressor operates on R134a. The inlet to the compressor is saturated vapor at −20°C. The outlet of the compressor is at 7.7 bar and $\eta_C = 0.8$. Find the reversible and required work (kJ/kg) and the outlet temperature of the compressor.

Solution: An inset of the *P-H* diagram from Appendix E is shown below. The axis labels and superheated temperature labels have been translated on the inset diagram.

The inlet state is located at the intersection of the −20°C isotherm and the saturated vapor line. The enthalpy is found by following the vertical lines to the axis and $H = 386.5$ kJ/kg. (Note: This accurate value was found from the accompanying saturation table, but the schematic value is consistent, though less accurate.) The reversible outlet state is found by following an isentropic state up to 7.7 bars. One set of the diagonal lines are isentropes, and we visually interpolate to keep the same relative position between the isentropes at 7.7 bar at the state labeled 2'. By following the vertical lines to the axis, $H_2' = 424$ kJ/kg. The reversible work is $W_S' = 424 − 386.5 = 37.5$ kJ/kg. The actual work is $W_S = W_S' / 0.8 = 47$ kJ/kg. The actual outlet state is shifted to the right at 7.7 bar at an enthalpy value of $H_2 = 386.5 + 47 = 433.5$ kJ/kg. The reversible outlet is just near 38°C. The actual outlet is near 48°C.

Before beginning more examples, it is also helpful to keep in mind those processes which generate entropy. This is important because, in the event that such processes arise, the entropy-generation term cannot be set to zero unless we modify the process to eliminate the source of the generation. Entropy is generated by the following processes.

1. Heat conduction along a temperature gradient.

2. Diffusion along a concentration gradient.

3. Mixing of substances of different composition.

4. Adiabatic mixing at constant system volume of identical substances initially at different molar entropies due to (T, P) differences.

5. Velocity gradients within equipment. This is accounted for in pipe flow by the friction factor developed in textbooks on fluid flow.

6. Friction.

7. Electrical resistance.

8. Chemical reactions proceeding at measurable rates.

In an open system, irreversibilities are always introduced when streams of different temperatures are mixed at constant pressure (item 4 above) because we could have obtained work by operating a heat engine between the two streams to make them isothermal before mixing. If the streams are isothermal, but of different composition, mixing will still generate entropy (e.g., see Eqn. 4.8 on page 138), and we have not yet devised a general method to obtain work from motion on this molecular scale.

As chemical engineers, it is important to recognize that all chemical reactions proceeding at a finite rate generate entropy. The fundamental proof of this is provided in Section 17.16 and requires

4.12 OPTIMUM WORK AND HEAT TRANSFER

Let us consider how to calculate the optimum work interactions for a general system. For an open system where kinetic energy and potential energy changes are negligible,

$$dU = \sum_{inlets} H^{in} dn^{in} - \sum_{outlets} H^{out} dn^{out} + dQ - PdV + dW_S \qquad 4.50$$

$$dS = \sum_{inlets} S^{in} dn^{in} - \sum_{outlets} S^{out} dn^{out} + \frac{dQ}{T_{sys}} + dS_{gen} \qquad 4.51$$
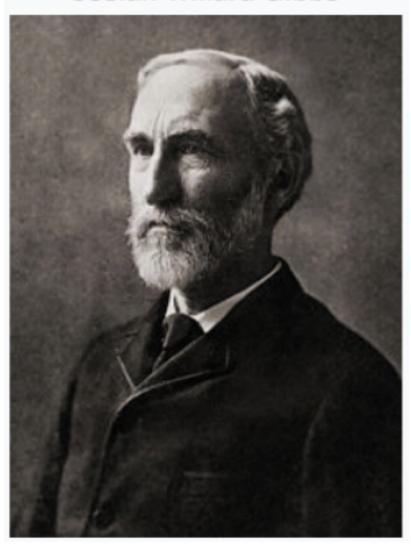
where $dS_{gen} = 0$ for an internally reversible process. If all the heat is transferred at a single temperature T_{sys}, elimination of dQ in the first balance provides

$$dU = \sum_{inlets} (H^{in} - T_{sys}S^{in}) dn^{in} - \sum_{outlets} (H^{out} - T_{sys}S^{out}) dn^{out} \qquad 4.52$$

$$+ T_{sys}dS - PdV + dW_S - T_{sys}dS_{gen}$$

Josiah Willard Gibbs

$$dU = TdS - p\,dV + \sum_i \mu_i\,dN_i$$

where T is the absolute temperature, p is the pressure, dS is an infinitesimal change in entropy and dV is an infinitesimal change of volume. The last term is the sum, over all the chemical species in a chemical reaction, of the chemical potential, μ_i, of the ith species, multiplied by the infinitesimal change in the number of moles, dN_i of that species. By taking the Legendre transform of this expression, he defined the concepts of enthalpy, H and Gibbs free energy, G.

$$G_{(p,T)} = H - TS$$

This compares to the expression for Helmholtz free energy, A.

$$A_{(v,T)} = U - TS$$

When the Gibbs free energy for a chemical reaction is negative the reaction will proceed spontaneously. When a chemical system is at equilibrium, the change in Gibbs free energy is zero. An equilibrium constant is simply related to the free energy change when the reactants are in their standard states.

$$\Delta G^{\ominus} = -RT \ln K$$

Chemical potential is usually defined as partial molar Gibbs free energy.

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j \neq i}}$$

tesimal temperature differences will be infinitesimally slow. The surrounding's temperature and pressure (T_o and P_o) are often considered the **dead state,** because when the system reaches this T and P, energy input of some type is necessary to obtain expansion/contraction work, shaft work, or heat transfer; without energy input the process is dead. However, departures from this dead state *do* provide opportunities for work and heat interactions. Further, it is desirable to give a name to the combination of variables that results. For the combination of variables in the summations of Eqn. 4.52 modified with T_o, we will use the term **availability,** or **exergy,** B,

$$B = H - T_o S \quad \text{availability or exergy} \qquad 4.53$$

where H and S are state properties of the system at T and P, but T_o is the temperature of the dead state. The terms "availability" and "exergy" are both used in literature for this property. At a given T and P, the availability changes with T_o, so B is somewhat different from other state properties used to this point. Inserting the availability into Eqn. 4.52, and collecting the state changes of the system on the left-hand side, results in a general balance (ignoring kinetic and potential energy like before),

$$d\underline{U} + Pd\underline{V} - T_o d\underline{S} = \sum_{\text{inlets}} (B^{in}) dn^{in} - \sum_{\text{outlets}} (B^{out}) dn^{out} + d\underline{W}_S - T_o d\underline{S}_{gen} \qquad 4.54$$

A potential for every thermodynamic situation [edit]

In addition to U and $U[\mu]$, the other thermodynamic potentials are frequently used to determine exergy. For a given set of chemicals at a given entropy and pressure, enthalpy H is used in the expression:

$$B = H - T_R S \qquad (5)$$

For a given set of chemicals at a given temperature and volume, Helmholtz free energy A is used in the expression:

$$B = A + P_R V \qquad (6)$$

For a given set of chemicals at a given temperature and pressure, Gibbs free energy G is used in the expression:

$$B = G \qquad (7)$$

The potentials A and G are utilized for a constant temperature process. In these cases, all energy is free to perform useful work because there is no entropic loss. A chemical reaction that generates electricity with no associated change in temperature will also experience no entropic loss. (*See Fuel cell.*) This is true of every isothermal process. Examples are gravitational potential energy, kinetic energy (on a macroscopic scale), solar energy, electrical energy, and many others. If friction, absorption, electrical resistance or a similar energy conversion takes place that releases heat, the impact of that heat on thermodynamic potentials must be considered, and it is this impact that decreases the available energy.

Applications [edit]

Applying equation (1) to a subsystem yields:

$$\text{If } \frac{dB}{dt} \begin{cases} > 0, & \frac{dB}{dt} = \text{maximum power generated} \\ < 0, & \frac{dB}{dt} = \text{minimum power required} \end{cases} \qquad (14)$$

This expression applies equally well for theoretical ideals in a wide variety of applications: electrolysis (decrease in G), galvanic cells and fuel cells (increase in G), explosives (increase in A), heating and refrigeration (exchange of H), motors (decrease in U) and generators (increase in U).

$$\frac{dB}{dt} \le 0 \text{ is equivalent to } \frac{dS_{total}}{dt} \ge 0 \qquad (1)$$

One goal of energy and exergy methods in engineering is to compute what comes into and out of several possible designs before a factory is built. Energy input and output will always balance according to the First Law of Thermodynamics or the energy conservation principle. Exergy output will not balance the exergy input for real processes since a part of the exergy input is always destroyed according to the Second Law of Thermodynamics for real processes. After the input and output are completed, the engineer will often want to select the most efficient process. An energy efficiency or *first law efficiency* will determine the most efficient process based on wasting as little energy as possible relative to energy inputs. An exergy efficiency or *second-law efficiency* will determine the most efficient process based on wasting *and destroying* as little available work as possible from a given input of available work.

Design engineers have recognized that a higher exergy efficiency involves superior design and often leads to a higher return on investment. For example, in the case of allocating roof space for solar energy collection between thermal systems and photovoltaic technology, photovoltaic thermal hybrid solar collector technology provide the highest exergy efficiency and optimized solution.[3]

Steady-State Flow

For a system at steady-state flow, all terms on the left-hand side drop out, resulting in

$$\sum_{outlets} (B^{out})dn^{out} - \sum_{inlets} (B^{in})dn^{in} = d\underline{W}_S - T_o d\underline{S}_{gen} \quad \text{steady-state open system} \qquad 4.55$$

and we conclude that the difference in availability from the inlets to outlets is related to the optimum shaft work. Note that $T_o d\underline{S}_{gen} \geq 0$ and always subtracts from work input when $d\underline{W}_S \geq 0$ which means work input for an irreversible process is always greater than a reversible process for a given

Closed System

For a closed system, Eqn. 4.54 becomes

$$d\underline{U} + Pd\underline{V} - T_o d\underline{S} = d\underline{W}_S - T_o d\underline{S}_{gen} \quad \text{closed system} \qquad 4.57$$

For a constant-pressure closed system, $\underline{V}dP$ can be added to the left side (because it is zero in magnitude), which then results in $d\underline{U} + Pd\underline{V} + \underline{V}dP = d\underline{U} + d(P\underline{V}) = d\underline{H}$. Thus, the left-hand side can be replaced with $d\underline{B}$, though it is usually easier to calculate $d\underline{H}$ and $T_o d\underline{S}$ independently. We can define the **Gibbs energy** $G \equiv H - TS$. Then $dG = dU + PdV + VdP - TdS - SdT$. Thus, if the pressure is constant *and* the temperature is constant at T_o, then the change in Gibbs energy is related to the non-expansion/contraction work. Another interesting analysis can be done if both work terms are on the right-hand side of the equation:

$$d\underline{U} - T_o d\underline{S} = d\underline{W}_S - Pd\underline{V} - T_o d\underline{S}_{gen} \quad \text{closed system} \qquad 4.58$$

We can define the **Helmholtz energy** $A \equiv U - TS$. Then $dA = dU - TdS - SdT$. When the system is isothermal at T_o, then the change in Helmholtz energy is related to the sum of all forms of work.

Example 4.18 Minimum heat and work of purification[a]

Products produced by biological systems can range over mole fractions from 10^{-1} to 10^{-9}.

(a) Estimate the minimum reversible heat and work requirement to purify one mole of product at 298.15 K over this range.
(b) To understand the concentrations in dilute mixtures, calculate the mole fraction of insulin in 0.1wt% aqueous solution.

Solution: The work is from Eqn. 4.67, and the heat will have the opposite sign.

$$\frac{-RT(x_1 \ln x_1 + x_2 \ln x_2)_F}{x_2} = \frac{\dot{W}_s}{\dot{n}_2}$$

For $x_2 = 0.10$, $x_1 = 0.9$. At 298.15K,
$\dot{W}_s/\dot{n}_2 = -8.314(298.15)(0.1\ln(0.1) + 0.9\ln(0.9)) / 0.1 = 8.1kJ$

Repeating the calculation for other values of x_2:.

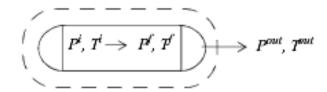| x_2	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
$\dot{W}_s/\dot{n}_2$ (kJ/mol)	8.1	13.9	19.6	25.3	31.0	36.7	42.4	48.1	53.8

Note that heat must be rejected. If a process is envisioned that requires heat, then the rejected heat must be increased by an equal amount. For example, if a solution of concentration $x_2 = 0.10$ is purified by adding 1 kJ of heat, then 9.1 kJ must be rejected.

(b) Searching for the molecular weight of insulin reveals a value of 5808 g/mol. Therefore, $x_1 = 0.001/5808 = 1.72(10^{-7})$. The point is that biomolecules are often large, and therefore their concentrations can be quite small on a mole fraction basis.

4.14 UNSTEADY-STATE OPEN SYSTEMS

Example 4.19 Entropy change in a leaky tank

Consider air (an ideal gas) leaking from a tank. How does the entropy of the gas in the tank change? Use this perspective to develop a relation between T^f and P^f and compare it to the expression we obtained previously by the energy balance.

Solution:

m-Balance: $dn = -dn^{out}$

S-Balance: $\dfrac{d(nS)}{dt} = -S^{out}\dfrac{dn^{out}}{dt} \Rightarrow ndS + Sdn = -S^{out}dn^{out}$

But physically, we know that the leaking fluid is at the same state as the fluid in the tank; therefore, the S-balance becomes $ndS + \cancel{Sdn} = -S^{out}\cancel{dn^{out}}$, or $\Delta S = 0$.

For an ideal gas with a constant heat capacity:

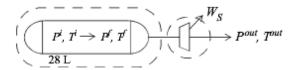$$\Delta S = C_V \ln(T_2/T_1) + R\ln(V_2/V_1) = 0 \qquad (\text{*ig})$$

$$\Delta S = C_V\ln(T_2/T_1) + R\ln((T_2 P_1)/(P_2 T_1)) = (C_V + R)\ln(T_2/T_1) - R\ln(P_2/P_1) \qquad (\text{*ig})$$

$$(T_2/T_1) = (P_2/P_1)^{(R/C_p)} \qquad (\text{*ig})$$

Compare with Example 2.15 on page 81. The entropy balance and energy balance in this case are not independent. Either can be used to derive the same result. This also shows that our analysis in Example 2.15 was assumed to be reversible.

Example 4.20 An ideal gas leaking through a turbine (unsteady state)

A portable power supply consists of a 28-liter bottle of compressed helium, charged to 13.8 MPa at 300 K, connected to a small turbine. During operation, the helium drives the turbine continuously until the pressure in the bottle drops to 0.69 MPa. The turbine exhausts at 0.1 MPa. Neglecting heat transfer, calculate the maximum possible work from the turbine. Assume helium to be an ideal gas with $C_P = 20.9$ J/mol-K.

Consider a balance on the *tank only*. The result of the balance will match the result of Example 4.19.

Writing an entropy balance for a reversible adiabatic *turbine only*,

$$(S^{out} - S^{in})\dot{n} = 0 \Rightarrow \Delta S = 0$$

which shows that the turbine also does not change the molar entropy. Thus, the molar entropy of the exiting fluid is the same as the entropy in the tank, which is identical to the molar entropy at the start of the process. Therefore, the molar entropy and the pressure of the exiting gas are fixed. Since only two intensive properties fix all other intensive properties for a pure fluid, the exiting temperature is also fixed. The relation for an ideal gas along a reversible adiabat gives:

$$T^{out} = T^i (P^{out} / P^i)^{R/C_P} = 42.3 \text{ K} \tag{*ig}$$

Likewise: $T^f = T^i (P^f / P^i)^{R/C_P} = 91.1 \text{ K}$ (*ig)

Solution by overall energy balance:

$d(nU) = H^{out} dn + d\underline{W}_S$ and H^{out} is fixed since T^{out}, P^{out} are fixed; therefore, we may apply hint 4(a) from Section 2.14.

Integrating this expression:

$$n^f U^f - n^i U^i = H^{out}(n^f - n^i) + \underline{W}_S$$

Rearranging:

$$\underline{W}_S = n^f(U^f - H^{out}) - n^i(U^i - H^{out}) \tag{4.70}$$

Determining variables in the equation:

$$n^f = P^f \underline{V}/RT^f; \ n^f = 25.5 \text{gmol}; \ n^i = 154.9 \text{ gmol} \tag{ig}$$

Choose reference temperature, $T_R \equiv 300$ K, $\Rightarrow$ setting $U_R = 0$, then since $H_R = U_R + (PV)_R$, and since the fluid is an ideal gas, $C_V = C_P - R = 20.9 - 8.314 = 12.586$ J/mol-K:

$$H_R = (PV)_R = RT_R = R(300) \tag{ig 4.71}$$

Note: $\Rightarrow H(T) = C_P(T - T_R) + H_R = C_P(T - 300) + R(300)$ (*ig)

$$H^{out} = -2892 \text{ J/mol} \tag{*ig}$$

$$U^f = C_V(T - T_R) + U_R = -2629 \text{ J/mol}; \ U^i = 0 \tag{*ig}$$

Now, plugging into Eqn. 4.70:

$$\underline{W}_S = 25.5(-2629 + 2892) - 154.9(0 + 2892)$$

$$\Rightarrow \underline{W}_S = -441,200 \text{ J}$$