
4200:225 Equilibrium Thermodynamics

Unit I. Earth, Air, Fire, and Water

Chapter 3. The Entropy Balance

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Unit I. Energy and Entropy

Chapter 3. The Entropy Balance

Introduction to Entropy

Microscopic definition: $dS = k \ln(p_2/p_1)$

Macroscopic definition: $dS = Qdt/T$

Macrostate

Box A	Box B	# Microstates	Probability of Macrostate
0	2	1	0.25
1	1	2	0.50
2	0	1	0.25
		$4=2^2$	

	Atom	
	1	2
B	A	A
o	B	A
x	A	B
	B	B

All of these microstates are “distinguishable”, because *there is no question of which particle went into Box A first when there is only one particle in Box A.*

Indistinguishable microstates: We can tell where the particles are but we don't know when they got there. Thermodynamics does not care about time (except when you need to be quick on the test).

Consider 5 particles distributed between two boxes. Similar to 2 particles we have:

BBAAA	ABBAA	AABBA	AAABB
BABAA	ABABA	AABAB	
BAABA	ABAAB		
BAAAB			

In order to treat 10^{23} particles, we need a more general mathematical approach. Consider the case of two particles in Box B. There are 20 ways of this happening: 5 ways of picking the first particle plus 4 ways of picking one of the remaining particles. But why does the above table show only 10?

ANS: Only 10 are “distinguishable”. e.g. For the case of particles 2 and 5 in box B, we could distinguish between whether particle 2 came first or particle 5 came first, **if we followed the process over time**. But if we only look at the result, then all we can say is that particles 2 and 5 are in the box and we don't know how they got there. Looking at it in this way, we see that there are only 10 ways of having 2 particles in Box B.

We do not distinguish between, e.g. B_1B_2AAA vs. B_2B_1AAA or AB_1AAB_2 vs. AB_2AA
 B_1

I. Energy and Entropy

Macrostate

Box A	Box B	# Microstates	Probability of Macrostate
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
		$32=2^5$	

N ways of
 $N(N-1)$
 $N(N-1)(N-2)$
 $N!/(N-m)!$

1 particle in Box B
 2 particles in Box B
 3 particles in Box B
 m particles in Box B

2 ways **indist** for 2 particles in Box B
 $2*3$
 $2*3*4$
 $m!$

3
 4
 m

In General:

$$p_j = \frac{N_j!}{m_j!(N_j - m_j)!} \quad \text{for two boxes.}$$

$$p_j = \frac{N_j!}{\prod_{i=1}^M m_{ij}!} \quad \text{for } M \text{ boxes.}$$

I. Energy and Entropy

Example 3.1. Entropy change vs. volume change

$$p_1 = \frac{N_o!}{N_o!O!} = 1 \quad ; \quad p_2 = \frac{N_o!}{(N_o/2)!(N_o/2)!}; \quad \ln(p_2/p_1) = \ln \left(\frac{N_o! / (N_o/2)!^2}{1} \right)$$

$$\Delta S = S_2 - S_1 = k \ln(p_2 / p_1) = k \{ \ln(N_o!) - 2 \ln[(N_o / 2)!] \}$$

Stirling's approximation: $\Rightarrow \ln(N!) = N \ln(N) - N$ for large N

$$\begin{aligned} \Rightarrow \Delta S &= k [N_o \ln(N_o) - N_o - 2(N_o / 2) \ln(N_o / 2) + 2(N_o / 2)] \\ &= k [N_o \ln(N_o) - N_o - N_o \ln(N_o) + N_o \ln(2) + N_o] \\ &= k N_o \ln(2); \text{ Noting that } N_o k \equiv nR \quad \Rightarrow \Delta S = nR \ln(2) \end{aligned}$$

I. Energy and Entropy

Example 3.1 (cont.). Entropy change vs. volume change

Suppose the box with particles is three times as large as the empty box. Then what is the entropy change? The trick is to imagine a number of equal size boxes.

$$p_1 = \frac{N_o!}{\left(\frac{N_o!}{3}\right)^3 O!} = 1 \quad ; \quad p_2 = \frac{N_o!}{[(N_o/4)!]^4} ; \quad \ln(p_2/p_1) = \ln\left(\frac{[(N_o/3)!]^3}{[(N_o/4)!]^4}\right)$$

$$3 \ln[(N_o/3)!] = 3 \{(N_o/3) \ln((N_o/3)) - (N_o/3)\} = N_o \ln(N_o/3) - N_o$$

$$4 \ln[(N_o/4)!] = 4 \{(N_o/4) \ln((N_o/4)) - (N_o/4)\} = N_o \ln(N_o/4) - N_o$$

$$\Delta S = kN_o [\ell n(N_o/3) - \ell n(N_o/4)] = nR \ln(4/3) = nR \ln(V_2/V_1)$$

I. Energy and Entropy

Example 3.2. Entropy change of mixing ideal gases

One mole of pure oxygen and 3 moles of pure nitrogen are mixed at constant T and P . Determine the entropy change. You may treat O_2 and N_2 as ideal gases for this calculation.

Solution: If the oxygen and nitrogen act as ideal gases, then they have no interaction energy with each other. They are simply point masses that can't see each other. This means that the entropy changes can be calculated independently for each.

$$\text{For } O_2: \quad \Delta \underline{S}_{O_2} = n_{O_2} R \ln(4) = n_{\text{tot}} R [-x_{O_2} \ln(0.25)] = n_{\text{tot}} R [-x_{O_2} \ln(x_{O_2})]$$

$$\text{For } N_2: \quad \Delta \underline{S}_{N_2} = n_{N_2} R \ln(4/3) = n_{\text{tot}} R [-x_{N_2} \ln(0.75)] = n_{\text{tot}} R [-x_{N_2} \ln(x_{N_2})]$$

$$\text{Total:} \quad \Delta \underline{S}_{\text{tot}} = -n_{\text{tot}} R [x_{O_2} \ln(x_{O_2}) + x_{N_2} \ln(x_{N_2})]$$

$$\text{Answer:} \quad \Delta \underline{S}_{\text{tot}} = -4 R [0.25 \ln(0.25) + 0.75 \ln(0.75)] = -4 * 8.314 * (-0.562) = 18.7 \text{ J/K}$$

Note: In general, ideal mixing $\Rightarrow \Delta S_{\text{tot}} = -R * \sum x_i \ln(x_i)$. How would you use the macroscopic definition of entropy to derive this result? What would be the reversible process and how would heat be involved?

Example 3.3 Entropy Changes for an Ideal Gas in a Piston+Cylinder

(1) Suppose an ideal gas in a piston+cylinder is isothermally and reversibly expanded to twice its original volume. What will be the amount of heat added? What does this suggest about changes in entropy with respect to heat addition?

$$\text{E-bal: } Q^{\text{rev}} = -W^{\text{rev}} = + \int PdV = RT \int dV/V = RT \ln(V_2/V_1)$$

$$\text{S-bal: Microscopic definition: particles at constant } T \Rightarrow \Delta S = R \ln(V_2/V_1)$$

$$\text{Comparing shows that } Q^{\text{rev}} = T\Delta S \Rightarrow dS = \dot{Q}^{\text{rev}} dt / T$$

Thus we have inferred the macroscopic definition of entropy from the microscopic definition.

We can now apply whichever definition is most convenient for a given problem.

(2) Suppose the above expansion had been carried out reversibly but adiabatically. Then what would be the relation between the temperature and volume, and how would the entropy change?

$$\text{E-bal: } d(nU) = \dot{W} dt \Rightarrow ndU = -PdV \Rightarrow dU = -PdV = -RT dV/V = C_V dT$$

$$\Rightarrow C_V \ln(T_2/T_1) = -R \ln(V_2/V_1)$$

$$\text{S-bal: MACROscopic definition: } \Delta S = 0$$

Rearranging the energy balance gives us a general relationship for any change in an ideal gas.

Comparing the equation below to the previous two examples shows that all are described by:

$$dS^{\text{ig}} = C_V dT/T + R dV/V$$

Note: Assuming a constant heat capacity, and noting $PV=RT$ for an ideal gas:

$$\Delta S^{\text{ig}} = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) = C_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

This equation provides the starting point for much of our discussion in Unit II.

Example 3.6. Entropy Generation for an Ideal Gas in a Piston+Cylinder

Suppose the expansion were carried out adiabatically but irreversibly, such that no work was derived. What would be the final temperature and how much potentially useful work would have been lost?

$$\text{E-Bal: } d(nU) = \underline{Q} + \underline{W} = 0 + 0 = nC_v dT \Rightarrow dT=0 \Rightarrow T_f = T_i .$$

$$\text{S-Bal: Microscopic definition at constant } T: \Delta S = R \ln(V_2/V_1)$$

As for the lost work, a reversible expansion with $T_f = T_i$ would yield: $W = -RT \ln(V_2/V_1)$

Comparing the expression for lost work to the expression for entropy change:

$$\text{Lost work} = |W| = -RT \ln(V_2/V_1) = T\Delta S \equiv T S_{gen}$$

where S_{gen} is the entropy generated by conducting the process irreversibly.

$$dS = \frac{\dot{Q}^{rev} dt}{T} + S_{gen}$$

for any process, noting that $S_{gen} \geq 0$.

Example 3.5 Simple Entropy Generation According to the Macroscopic Definition

A 500 ml glass of chilled water at 283 K is removed from a refrigerator and warmed to 298 K. Calculate the entropy change of the water, the surroundings, and the universe.

Solution:

In this problem, each subsystem can be treated as being reversible, then the sum over subsystems gives the total change. Since the heat flows are obvious, it is straightforward to apply the macroscopic definition.

Water: Macroscopic definition $\Rightarrow dS = dQ_{rev}/T$

E-bal: $dQ_{rev} = dH = Cp dT$ (const P heating, cf. Eqn 3.11)

$$\Delta S_{water} = \int mCp dT/T = mCp \ln(T^f/T^i) = 500*4.184*\ln(298/283) = 108 \text{ J/K}$$

Surroundings: Note the temperature of the surroundings is not significantly affected by this process, but the heat can only come from the water (E-bal tells us so).

$$\Rightarrow \Delta S_{surr} = \int dQ_{rev}/T_{surr} = -500*4.184*(298-283)/298 = -31,380/298 = -105.3 \text{ J/K}$$

Universe: $\Delta S_{total} = \Delta S_{water} + \Delta S_{surr} = 2.7 \text{ J/K} > 0 \Rightarrow$ irreversible

NOTE! Temperature gradients cause irreversibilities as do u - gradients, P -gradients...

I. Energy and Entropy

THE COMPLETE ENTROPY BALANCE

$$\frac{dS}{dt} = \sum \dot{m}_k S_k + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

Note:

1. S_{gen} must generally be back-calculated after treating the reversible process and comparing to the actual process. Therefore, we start most problems with $S_{gen} = 0$
2. The microscopic definition of entropy is not here. It is necessary to understand the nature of entropy and mixing processes, but it is not generally convenient for the kinds of process calculations in Unit I.
3. In most cases of interest, $\Delta S^{rev} = 0$. e.g. turbine, compressor, piston. (Write this first, then check the problem statement to see if it is true.)
4. In heat exchange: $\Delta S = Q/T$. If condensing, $\Delta S = \Delta H_{vap} * \Delta q/T$. e.g. boilers, condensers.
5. Rare but often overlooked: $\Delta S^{rev} = Q/T$. e.g. isothermal compressor.

I. Energy and Entropy

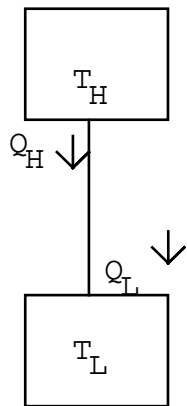
~Example 3.5gen. Entropy generation in a temperature gradient - general formula

Suppose there are two heat reservoirs, one at a temperature T_H and a second at a lower temperature T_L . Let a quantity of energy Q be transferred as heat from the high-temperature reservoir to the low-temperature reservoir. We can imagine that the heat leaving at T_H occurs by a reversible process as does the heat entering at T_L , but we do not specify what happens in between. What happens to the entropy? (You may assume that the two heat reservoirs are large enough that there is no temperature change in either reservoir.)

Solution $\Delta S_1 = Q_H/T_H$; $\Delta S_2 = Q_L/T_L$;

Energy balance: $Q_H = -Q_L$; No work is accomplished.

$$\Delta S_{tot} = \frac{-Q_L}{T_H} + \frac{Q_L}{T_L} = Q_L \frac{T_H - T_L}{T_H T_L} = -Q_H \frac{T_H - T_L}{T_H T_L}$$

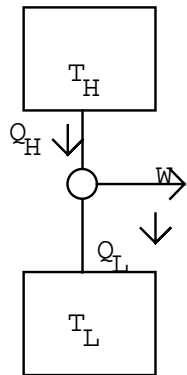


Note: If $T_H > T_L$ and no work is accomplished, then $\Delta S_{tot} > 0$. (It could not be less than zero because heat cannot flow from a lower temperature to a higher temperature without adding work.) This observation is basically one way of stating the second "law" of thermodynamics.

Example 3.8. Reversible work between heat reservoirs

A reversible heat engine absorbs 1000 J at a constant temperature of 500°C, produces work, and discards heat at 100°C. Don't worry for now about the machinations that make this possible. They basically involve some turbines and compressors and heat exchangers to be discussed in detail in Chapter 4. Considering simply the overall entropy changes, what is the change in entropy of the heat source and the heat sink and what is the total entropy change resulting from the process? How much work is produced?

Solution.



Energy Balance: (on engine): $W = -Q_{net} = -(Q_{in} + Q_{out}) = -(-Q_H - Q_L)$

Entropy Balance: $\Delta S_{tot} = 0$ (reversible)

(This process is different from the previous example because $Q_L \neq -Q_H$)

$$\Delta S_1 = Q_H/T_H = -1000 \text{ J} / 773^\circ\text{K} = -1.29 \text{ J/K}$$

$$\Delta S_2 = 1.29 \text{ J/K} = Q_L/T_L \Rightarrow Q_L = 481$$

$$\Rightarrow W = -(1000 - 481) = -518 \text{ J}$$

Note:
$$W^{rev} = -Q_H \frac{T_H - T_L}{T_H} = T_L \left[-Q_H \frac{T_H - T_L}{T_H T_L} \right]$$

We don't need to specify the mechanical details since an overall balance suffices. If you want to know, however, a "Carnot" cycle would give this result. A typical Carnot cycle

is: (1) boiling at high temperature (2) isentropic turbine (3) condensation at low temperature (4) isentropic compression back to saturated liquid at state 1.

I. Energy and Entropy

Example 3.11. Heat pump analysis

It is proposed to heat a building using a heat pump. The average outdoor temperature is 40°F and the indoors is to be maintained at 70°F. The temperature difference between the fluid inside the coils and the air is 10°F, indoors and out. What would be the maximum cost of electricity in (\$/kW-hr) for which the heat pump would be competitive with conventional heating where a fuel is directly burned for heat. In the latter method, the cost is \$7.00 per million Btu. (Consider only energy costs. 1kW = 56.9 Btu/min).

Solution Entropy Balance $\Delta S = 0$

$$W = Q_1 \frac{(30 - 80)}{(80 + 460)} = \frac{-50}{540} * Q_1 \left(\frac{\text{Btu}}{\text{min}} \right) \left(\frac{1\text{kW}}{56.9 \text{ Btu}/\text{min}} \right)$$

Heat pump cost = $(5/54)(Q_1/56.9)(\theta \text{ hr}) [x \text{ \$/kw-hr}]$;

Direct heating cost = $Q_1 (60 \text{ min/hr}) \theta \text{ hr } \$7/(10^6 \text{ Btu})$

For maximum, let heat pump cost = direct heating cost

$$\Rightarrow (5/54) Q\theta/56.9 x = Q\theta 7*60/10^6 \Rightarrow x = \$0.258/\text{kw-hr} ;$$

actual cost 2/13/88 ~ \$0.10/kW-hr therefore might use heat pump if COP ~ Carnot

Example 3.10 Turbine Efficiency

Steam is supplied to a steady state turbine at 1.35 MPa and 375°C. In the actual process, the discharge from the turbine at 0.01 MPa was saturated vapor only. Determine the efficiency of the turbine, the lost work and the effective temperature at which the lost work was lost.

$$\eta = \Delta H / \Delta H^{rev} = W^{act} / W^{rev}$$

Initially, $H_{1.35}^{375C} = 3205$ kJ/kg ; $S_{1.35}^{375C} = 7.2401$ kJ/kg-K (by double interpolation)

Energy balance: $W^{act} = \Delta H = H_{0.01MPa}^{sat} - 3205 = 2584.3 - 3205 = -620.7$ kJ/kg

Entropy balance: $\Delta S^{rev} = 0$

$$7.2382 = q'(8.1502) + (1-q')(0.6493)$$

$$\Rightarrow q' = \frac{(7.2401 - 0.6492)}{(8.1488 - 0.6492)} = 0.8788$$

e.g. Double Interpolation on Enthalpy

$T^{\circ}C$	$P(MPa)=1.2$	<u>1.35</u>	<u>1.4</u>
350	3154.2	3151.1	3150.1
375		3205	
400	3261.3	3258.9	3258.1

$$\Rightarrow H_f^{rev} = 0.8788(2583.9) + (1-0.8788)(191.8) = 2294$$
 kJ/kg $\Rightarrow W^{rev} = 2294 - 3205 = -911$

$$\Rightarrow \eta = -620.7 / -911 = 68\%$$

$$\text{Lost work} = -911 - (-620.7) = -290$$
 kJ/kg

$$S_{gen} = (S_f^{act} - 7.2401) = 8.1488 - 7.2401 = 0.91$$
 kJ/kg-K

$$T_0 = |\text{lost work}| / S_{gen} = 290 / 0.91 = 318.7$$
 K ~ 45.8 °C = $T^{sat}(0.01$ MPa)

That is, this lost work was lost at the temperature at which it was rejected downstream.

You can use this observation to solve $LW = T_2 S_{gen}$ directly (no quality necessary).

I. Energy and Entropy

Example 3.13. Entropy change in a leaky tank

Consider 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:

$$\text{S-Balance: } S^{out} n^{out} dt = d(nS) = ndS + Sdn$$

$$\text{M-Balance: } n^{out} dt = dn \Rightarrow S^{out} dn = ndS + Sdn$$

$$\text{But physically, we know } S^{out} = S \Rightarrow S^{out} dn = Sdn \Rightarrow ndS = 0$$

$\Rightarrow \Delta S = 0$ This much is true whether it is an ideal gas or not!

For an ideal gas:

$$\Delta S = C_V \ln(T_2 / T_1) + R \ln(V_2 / V_1) = 0$$

$$= C_V \ln(T_2 / T_1) + R \ln\left(\frac{T_2 P_1}{T_1 P_2}\right) = (C_V + R) \ln(T_2 / T_1) - R \ln(P_2 / P_1)$$

$$\Rightarrow T_2 / T_1 = (P_2 / P_1)^{R/C_p}$$

Example 3.14. An ideal gas leaking through a turbine

A portable power supply consists of a 28 liter bottle of compressed helium, charged to 13.8 MPa at 300K, connected to a small turbine. During operation, the He 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 $C_p/R = 5/2$.

	TANK	TURBINE	OVERALL
E-Bal:	$H_T dn = d(nU)$	$W dt = +(H_0 - H_T) n dt$	$W = -H_0 (n_f - n_i) + \Delta(nU)$
S-Bal:	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
	$T_T = T_i \left(\frac{P_T}{P_i} \right)^{R/C_p}$	$T_0 = T_T \left(\frac{P_0}{P_T} \right)^{R/C_p}$	(Note: $P_0 = 0.1$)

Solution by overall balance:

$$n_f = P_f V / RT_f; T_f = T_i (P_f / P_i)^{R/C_p} = 90.5 \text{ K}; n_f = 25.7 \text{ gmol}; n_i = 154.9 \text{ gmol}$$

Note: Overall entropy balance $\Rightarrow \Delta S = 0 \Rightarrow S_0 = \text{const.}$ and $P_0 = \text{const.} = 0.1 \text{ MPa}$

Therefore, $T_0 = \text{const.} = T_i (P_0 / P_i)^{R/C_p} = 41.8 \text{ K}$

Let $T_{ref} \equiv 300 \text{ K}$, then

$$W = -[C_p(41.8 - 300) + R \cdot 300](25.7 - 154.9) + 25.7 C_v(90.5 - 300) - 154.9 C_v(300 - 300)$$

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

Note: $U(300) \equiv 0 \Rightarrow H(300) = 0 + R \cdot 300 \Rightarrow H(T) = C_p(T - 300) + R \cdot 300$

Example (not in book). Single stroke of a steam engine

A steam engine basically consists of a piston and a 1m^3 cylinder connected to a high-pressure steam line. At the right moment, a valve is opened and steam flows into the cylinder, pushing the piston towards the far end of the cylinder. The air initially to the right of the piston can be assumed to be at 1 bar. Estimate the maximum work and the resulting quality after a single stroke of this process.

Solution

E-bal: $H^{in}dm + W = d(mU)$

S-bal: $\Delta S = 0$ (max work \Rightarrow rev)

For the process to be reversible, the pressure on the piston must always equal the supply pressure, and the entropy is also constant. Since two properties specify the state condition,

$U_f = U^{in}$ and $q = 100\%$.

In other words, $W = P\Delta V = (5 - 0.1) * 1\text{E}6 = 4.9 \text{ MJ}$.

50 bars, saturated vapor steam supply line

