Chapter 22 Problems: Linear Non-equilibrium Thermodynamics

1. For a closed system and PV work only, describe why the second, lost-work term in Eq. 22.1.5 always gives the change in entropy production as greater than zero for an isothermal process (established by contact of the system with the surroundings acting as a constant temperature bath).

Answer: The plan is to apply the reasoning in Sec. 13.1 to Eq. 22.1.5:

$$\frac{dS_{tot}}{dt} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right)\frac{đq}{dt} + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right)\frac{dV}{dt}$$

   The second term involving P, P_{ext}, and V relates the pressure of the system, P, to the external pressure, P_{ext}. The difference in pressure, $P - P_{ext}$, is the pressure gradient between the system and the surroundings. This PV term is always positive for a spontaneous process. For an isothermal process, with the system in contact with the surroundings acting as a constant temperature reservoir, $T = T_{surr}$ giving the first term as zero. Assume the pressure of the system is greater than the external pressure. The pressure gradient is then positive, $P - P_{ext} > 0$. Our experience shows that the system will expand in a spontaneous process giving $dV > 0$. The product of $(P - P_{ext})/T$ and dV is positive. Now, consider a process with the system pressure less than the external pressure, $P < P_{ext}$. The system will contract in a spontaneous process giving $dV < 0$. However, the pressure gradient is also negative, $P - P_{ext} < 0$, so the product of $(P - P_{ext})/T$ and dV is still positive. In either case, the entropy increases for these spontaneous isothermal processes, $dS > 0$. On the other hand, if the system pressure and the external pressure are equal, the pressure gradient is zero and the entropy change is zero, $dS = 0$, for an isothermal process. With no pressure gradient, the system is at equilibrium and no process occurs.

   The second term is often called the **lost work** term. The PdV portion gives the work done by a reversible process. The $P_{ext}dV$ portion gives the actual work done by the spontaneous process. The difference, $PdV - P_{ext}dV$, is always positive. The difference is the lost work between the reversible and real process. In other words, to "pay" for an increase in entropy, some work is lost.

2. Reproduce Figure 22.1.1. Use the parameters in the caption and assume that the heat capacity of coffee is that of pure water. Assume a density of 1.00 g mL^{-1}.

Answer: The plan is to use Eq. 7.2.18 to find the temperature difference and Eq. 22.1.7 to find the entropy production as a function of time.

   For convenience in the following table the entropy production is converted to mJ K^{-1} s^{-1} to enable a common axis with ΔT. The formula for the temperature difference in D10 is:
       =($D$6-$G$6)*EXP(-$G$4/$G$3*C10)
The formula for the entropy production in E10 is:
       =$G$4*($D$6-$G$6)^2/$G$6^2*EXP(-2*$G$4/$G$3*C10)*1000
The total entropy is determined by finite difference integration. F9 is set to zero. F10 is:
       =F9+E9*(C10-C9)/1000

where E9 is the height of the current "rectangle" and C10-C9 is the width of the rectangle and the integral is the sum of the areas of the preceding rectangles. F11 and subsequent cells in the column continues the pattern: F11 is:

=F10+E10*(C11-C10)/1000

A1	B	C	D	E	F	G	H
2							
3		$\mathcal{K}$	1.14	J s^{-1} K^{-1} m^{-1}	Cp	836.8	J K^{-1}
4		$\mathcal{A}$	0.015	m^2	$\mathcal{KA}/\delta$	5.7	J K^{-1}s^{-1}
5		δ	3.00E-03	m			
6		T$_o$	310	K	T$_{surr}$	298	K
7							
8	t (min)	t (sec)	ΔT (K)	dS$_{tot}$/dt (mJ K^{-1} s^{-1})	S$_{tot}$ (J K^{-1})		
9	0	0	12.000	9.243	0.000		
10	0.5	30	9.782	6.142	0.277		
11	1	60	7.974	4.081	0.462		
12	1.5	90	6.500	2.712	0.584		
13	2	120	5.299	1.802	0.665		
14	2.5	150	4.320	1.198	0.719		
15	3	180	3.521	0.796	0.755		
16	3.5	210	2.870	0.529	0.779		
17	4	240	2.340	0.351	0.795		

5. With reference to Table 13.7.1, evaluate the entropy production for isothermal reversible, isothermal irreversible, adiabatic reversible, adiabatic irreversible, and a constant pressure expansion of an ideal gas. For the irreversible expansions, assume a constant external pressure, P_{ext}. Assume a closed system with no chemical reactions. In each case, specify the forces and fluxes that are zero in each case.

Answer: Consider first dS$_{tot}$ and the overall change in the total entropy for a process. The forces are determined by the temperature and pressure gradients. The processes are summarized in the table below.

For an isothermal process the temperature gradient is zero: $\left(\dfrac{1}{T} - \dfrac{1}{T_{surr}}\right) = 0$

For an adiabatic process, đq = 0 and the heat flux is then zero, đq/dt = 0.

For a reversible process, P = P_{ext} and the pressure gradient is zero: $\left(\dfrac{P}{T} - \dfrac{P_{ext}}{T}\right) = 0$

For an isothermal expansion of an ideal gas against a constant external pressure, $P/T = nR/V$:

$$dS_{tot} = \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) dV = \frac{P}{T} dV - \frac{P_{ext}}{T} dV = \frac{nR}{V} dV - \frac{P_{ext}}{T} dV$$

and the PV work term integrates for an overall process to give:

$$\int dS_{tot} = \int_{V_1}^{V_2} \frac{nR}{V} dV - \int_{V_1}^{V_2} \frac{P_{ext}}{T} dV = nR \ln \frac{V_2}{V_1} - \frac{P_{ext}\Delta V}{T} \qquad \text{(isothermal, P = } P_{ext}\text{)}$$

For an adiabatic expansion of an ideal gas against a constant external pressure, dU = đw. For any process in an ideal gas dU = C$_v$dT. Then for a constant external pressure, C$_v$ dT = – P_{ext} dV. Solving for dV:

$$dV = -\frac{C_v}{P_{ext}} dT$$

Using this last equation and $P/T = nR/V$ in the entropy production gives:

$$dS_{tot} = \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) dV = \frac{P}{T} dV - \frac{P_{ext}}{T} dV = \frac{P}{T} dV - \frac{C_v}{P_{ext}} \frac{P_{ext}}{T} dT = \frac{P}{T} dV - \frac{C_v}{T} dT$$

Integrating gives: $\Delta S_{tot} = nR \ln \frac{V_2}{V_1} + C_v \ln \frac{T_2}{T_1}$ (irr.adiabatic)

Finally for the last process, a constant pressure expansion for a change in temperature from T_1 to T_2, the pressure gradient is zero leaving:

$$dS_{tot} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right) đq$$

For an ideal gas at constant pressure $đq = đq_p = C_p dT$ giving:

$$dS_{tot} = \left(\frac{C_p}{T} - \frac{C_p}{T_{surr}}\right) dT$$

Integrating the result for a constant T_{surr} gives:

$$\Delta S_{tot} = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{T_1}^{T_2} \frac{C_p}{T_{surr}} dT = C_p \ln \frac{T_2}{T_1} - \frac{C_p}{T_{surr}} \Delta T$$ (cst. P = P$_{ext}$)
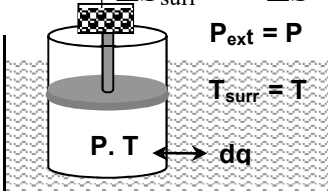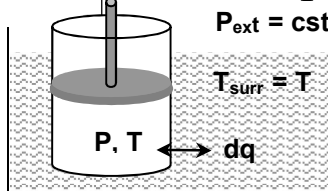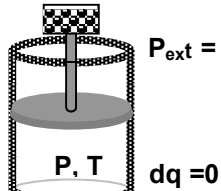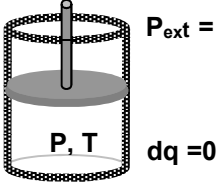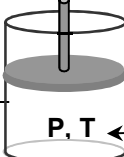
For the entropy production, instead of integrating over the complete process, the evolution of entropy is followed as a function of time:

$$\frac{dS_{tot}}{dt} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right) \frac{đq}{dt} + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) \frac{dV}{dt}$$

The result depends on the heat flux as a function of time and the volume change as a function of time. However, the final results are the same as given in the table and as derived above. Reversible processes give no entropy production. For an adiabatic process the heat flux is zero. For constant volume processes in closed systems the entropy production is entirely from the heat flux.

Entropy and the Surroundings – Ideal Gas

System	Surroundings	Universe $dS_{univ} = dS + dS_{surr}$
$dS = \dfrac{dU}{T} + \dfrac{P}{T}\,dV$	$dS_{surr} = -\dfrac{dq}{T_{surr}}$	$dS_{tot} = \left(\dfrac{1}{T} - \dfrac{1}{T_{surr}}\right)đq + \left(\dfrac{P}{T} - \dfrac{P_{ext}}{T}\right)dV$
$\Delta S = C_V \ln\dfrac{T_2}{T_1} + nR \ln\dfrac{V_2}{V_1}$ $\Delta S = C_P \ln\dfrac{T_2}{T_1} - nR \ln\dfrac{P_2}{P_1}$	$\Delta S_{surr} = -\dfrac{q}{T_{surr}}$	$\Delta S_{tot} = \Delta S + \Delta S_{surr}$

System	Surroundings	Universe $dS_{univ} = dS + dS_{surr}$
Isothermal reversible $T = T_{surr}$ $\Delta S = nR \ln\dfrac{V_2}{V_1}$ ($P_{ext} = P$, $T_{surr} = T$, P, T, dq)	$\Delta S_{surr} = -\Delta S$	$\Delta S_{tot} = 0$ $dS_{tot} = \left(\dfrac{1}{T} - \cancel{\dfrac{1}{T_{surr}}}^{\,0}\right)đq + \left(\dfrac{P}{T} - \cancel{\dfrac{P_{ext}}{T}}^{\,0}\right)dV$
Isothermal irreversible $T = T_{surr}$ $P_{ext} = cst$ $\Delta S = nR \ln\dfrac{V_2}{V_1}$ ($P_{ext} = cst$, $T_{surr} = T$, P, T, dq)	$\Delta S_{surr} = -\dfrac{P_{ext}\Delta V}{T}$	$\Delta S_{univ} = nR \ln\dfrac{V_2}{V_1} - \dfrac{P_{ext}\Delta V}{T}$ $dS_{tot} = \left(\dfrac{1}{T} - \cancel{\dfrac{1}{T_{surr}}}^{\,0}\right)đq + \left(\dfrac{P}{T} - \dfrac{P_{ext}}{T}\right)dV$
Adiabatic reversible $\Delta S = C_V \ln\dfrac{T_2}{T_1} + nR \ln\dfrac{V_2}{V_1}$ $= 0$ ($P_{ext} = P$, P, T, dq = 0)	$\Delta S_{surr} = 0$	$\Delta S_{tot} = 0$ $dS_{tot} = \left(\dfrac{1}{T} - \dfrac{1}{T_{surr}}\right)\cancel{đq}^{\,0} + \left(\dfrac{P}{T} - \cancel{\dfrac{P_{ext}}{T}}^{\,0}\right)dV$
Adiabatic irreversible $P_{ext} = cst$ $\Delta S = C_V \ln\dfrac{T_2}{T_1} + nR \ln\dfrac{V_2}{V_1}$ $C_V(T_2 - T_1) = -P_{ext}(V_2 - V_1)$ ($P_{ext} = cst$, P, T, dq = 0)	$\Delta S_{surr} = 0$	$\Delta S_{tot} = C_V \ln\dfrac{T_2}{T_1} + nR \ln\dfrac{V_2}{V_1}$ $dS_{tot} = \left(\dfrac{1}{T} - \dfrac{1}{T_{surr}}\right)\cancel{đq}^{\,0} + \left(\dfrac{P}{T} - \dfrac{P_{ext}}{T}\right)dV$ $dV = -\dfrac{C_v}{P_{ext}}\,dT$
Constant $P = P_{ext}$ $\Delta S = C_P \ln\dfrac{T_2}{T_1}$ ($P_{ext} = P$, P, T, dq)	$\Delta S_{surr} = -\dfrac{C_P\Delta T}{T_{surr}}$	$\Delta S_{tot} = C_P \ln\dfrac{T_2}{T_1} - \dfrac{C_P\Delta T}{T_{surr}}$