

ENTROPY AND SPONTANEOUS PROCESSES

Not all spontaneous processes are exothermic and not all exothermic processes are spontaneous

Entropy $\longrightarrow$ Measure of disorder

Non-equilibrium systems evolve to decrease their energy and increase their disorder.

Spontaneity depends on increasing disorder and decreasing energy.

Heat change for a reversible process:

$$\begin{aligned}\delta q_{\text{rev}} &= dU - \delta w_{\text{rev}} \\ &= C_V(T) dT + P dv\end{aligned}$$

For an ideal gas

$$\delta q_{\text{rev}} = \underset{\substack{\nearrow \\ \text{not a state} \\ \text{function}}}{C_V(T)} dT + \underset{\substack{\nearrow \\ \text{state function}}}{C_V(T)} dT + \underset{\substack{\nwarrow \\ \text{not a state} \\ \text{function}}}{\frac{nRT}{v}} dv$$

The right hand side of the equation does not represent an exact differential

The first term can be written as

$$C_v(T) dT = d \left[\int C_v(T) dT + A \right]$$

Since for an ideal gas $C_v(T)$ is only a function of T . Constant

The second term

$$\frac{nRT}{v} dv \neq d \left[\int \frac{nRT}{v} dv + B \right]$$

Since T depends on v

Dividing by T

$$\frac{\delta q_{rev}}{T} = \frac{C_v(T)}{T} dT + \frac{nR}{v} dv$$

↖ exact differential

So we may write

$$d\left[\int \frac{C_V(T)}{T} dT + nR \int \frac{dv}{v} + c\right]$$

$= \frac{\delta q_{rev}}{T}$

$\nearrow$
constant

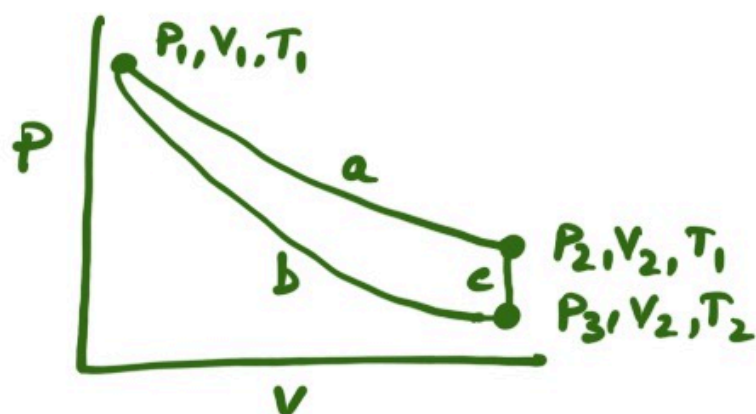
We define a term 'entropy' $\rightarrow S$

$$dS = \frac{\delta q_{rev}}{T}$$

Since S is a state function,
 $\Delta S = 0$ for a cyclic process

$$\Delta S = \oint \frac{\delta q_{rev}}{T} = 0$$

This is always true even though
we showed it only for an ideal
gas.



For path 'a'

Isothermal expansion from $V_1 \rightarrow V_2$

$$\Delta U_a = 0$$

$$\begin{aligned} q_{\text{rev},a} &= -w_{\text{rev},a} \\ &= nRT_1 \int_{V_1}^{V_2} \frac{dV}{V} \\ &= nRT_1 \ln \frac{V_2}{V_1} \end{aligned}$$

For path 'b'

Adiabatic expansion $V_1 \rightarrow V_2$

$$q_{\text{rev},b} = 0$$

For path 'c'

$$q_{\text{rev},c} = \int_{T_2}^{T_1} C_V(T) dT$$

Thus for path 'b' + 'c'

$$\begin{aligned} q_{\text{rev},bc} &= q_{\text{rev},b} + q_{\text{rev},c} \\ &= \int_{T_2}^{T_1} C_V(T) dT \end{aligned}$$

Since the temperature does not change for path 'b' + 'c', $\Delta U_{bc} = 0$

$$\delta w_{\text{rev},b} = -nRT \frac{dV}{V}$$

$$\delta w_{\text{rev},c} = 0$$

$$\delta w_{\text{rev},bc} = -\frac{nRT dV}{V}$$

$$\delta q_{\text{rev},bc} = -\delta w_{\text{rev},bc}$$

$$\int_{T_2}^{T_1} \frac{C_V(T)}{T} dT = nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S_{bc} = nR \ln\left(\frac{V_2}{V_1}\right)$$

Recall for path 'a'

$$q_{rev,a} = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

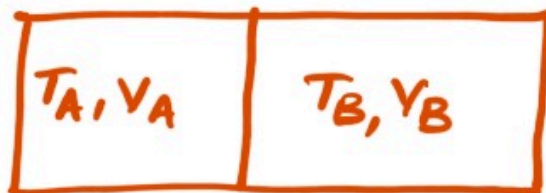
$$\Delta S_a = \frac{q_{rev,a}}{T_1} = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$= \Delta S_{bc}$$

ΔS is independent of path

→ S is a state function

Consider a system with two compartments.



Both systems are in equilibrium but not with each other

The composite system is isolated i.e. no heat or mass transfer can occur between the system and its surroundings.

We have

$$U_A + U_B \rightarrow \text{constant}$$

We also define

$$V_A \rightarrow \text{constant}$$

$$V_B \rightarrow \text{constant}$$

The total entropy

$$S = S_A + S_B$$

$$\begin{aligned} dU_A &= \delta q_{\text{rev},A} + \delta w_{\text{rev},A} \\ &= T_A dS_A \end{aligned}$$

$$\begin{aligned} dU_B &= \delta q_{\text{rev},B} + \delta w_{\text{rev},B} \\ &= T_B dS_B \end{aligned}$$

$$dS = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$$

Since $U_A + U_B$ is constant

$$dU_A + dU_B = 0 \quad dU_A = -dU_B$$

$$ds = dU_B \left(\frac{1}{T_B} - \frac{1}{T_A} \right)$$

If $T_B > T_A$, heat flows from $B \rightarrow A$ and $dU_B < 0$, $ds > 0$

If $T_B < T_A$, heat flows from system $A \rightarrow B$ and $dU_B > 0$, $ds > 0$.

There is an increase of entropy in both cases.

$ds = 0$ when $T_A = T_B$ and the system is at equilibrium.

The entropy of an isolated system increases for a spontaneous process

→ Second Law of Thermodynamics

Since a reversible process remains at equilibrium at all times $dS = 0$

For a non-isolated system i.e. one that can exchange energy with its surroundings, for a spontaneous process:

$$dS = dS_{\text{proc}} + dS_{\text{exch}}$$

entropy change
due to the spontaneous
process

entropy change
due to heat
exchange with
the surroundings

$$dS = dS_{\text{proc}} + \frac{\delta q}{T}$$

For a reversible process

$$\delta q = \delta q_{\text{rev}} \quad dS_{\text{proc}} = 0$$

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

For a spontaneous process

$$dS_{\text{proc}} > 0$$

$$dS_{\text{exch}} = \frac{\delta q_{\text{irr}}}{T}$$

$$dS > \frac{\delta q_{\text{irr}}}{T} \quad \text{since } dS_{\text{proc}} > 0$$

Thus in general,

$$dS \geq \frac{\delta q}{T} \quad \text{Clausius Inequality}$$

The entropy of the universe is increasing.

Consider the following case:

An ideal gas at temperature T_1 and volume V_1 is allowed to expand into vacuum to a final volume V_2

Even though this is not a reversible process, we write

$$\Delta S = \int_1^2 \frac{\delta q_{\text{rev}}}{T_1} \quad \text{we are integrating over a reversible path}$$

$$\begin{aligned} \delta q_{\text{rev}} &= dU - \delta w_{\text{rev}} \\ &= 0 - \delta w_{\text{rev}} = -\delta w_{\text{rev}} \end{aligned}$$

↪ since the temperature is constant

$$\begin{aligned}\delta w_{\text{rev}} &= -P dV \\ &= -\frac{nRT_1 dV}{V}\end{aligned}$$

$$\frac{\delta q_{\text{rev}}}{T_1} = \frac{nR dV}{V}$$

$$\Delta S = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln\left(\frac{V_2}{V_1}\right) > 0$$

since $V_2 > V_1$

While we used a reversible path to calculate ΔS , the same value would be obtained for an irreversible isothermal expansion.

For an isolated system $\Delta S \geq 0$ applies to the system.

For a system that is not isolated, $\Delta S \geq 0$ applies to the system and the surroundings.

For a reversible isothermal expansion

$$\Delta S_{\text{sys}} = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{\text{surr}} = -nR \ln(V_2/V_1)$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ = 0$$

For the irreversible expansion,

$$\Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{total}} = nR \ln \frac{V_2}{V_1} + 0 \\ > 0$$

Consider the isothermal mixing of two ideal gases A and B

$$\Delta S_A = n_A R \ln \left(\frac{V_A + V_B}{V_A} \right) = -n_A R \ln \left(\frac{V_A}{V_A + V_B} \right)$$

$$\Delta S_B = n_B R \ln \left(\frac{V_A + V_B}{V_B} \right) = -n_B R \ln \left(\frac{V_B}{V_A + V_B} \right)$$

For an ideal gas

$$\Delta S_A = -n_A R \ln \left(\frac{n_A}{N} \right) \quad N = n_A + n_B$$

$$\Delta S_B = -n_B R \ln \left(\frac{n_B}{N} \right)$$

$$\frac{n_i}{N} = x_i \quad \{ i = A, B \} \text{ mole fraction}$$

Dividing both sides by N and setting

$$\bar{\Delta S} = \frac{\Delta S}{N}$$

we have

$$\bar{\Delta S} = R \{ -x_A \ln x_A - x_B \ln x_B \}$$

generalizing, we get

$$\bar{\Delta S} = -R \sum_i x_i \ln x_i$$

Note that $x_i < 1$, $\ln x_i < 0$

$x_i \ln x_i < 0$

$\bar{\Delta S}$ always > 0

Consider two objects at temperatures T_h and T_c ($T_h > T_c$) that are brought into thermal contact with the final temperature settling at T for the composite object.

There is no work done $W_{\text{rev}} = 0$

$$dS = \frac{\delta q_{\text{rev}}}{T} = \frac{dU}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v dT}{T} \quad T_f = \frac{T_h + T_c}{2}$$

$$\Delta S_h = \int_{T_h}^{T_f} \frac{C_v dT}{T} = C_v \ln \frac{T_h + T_c}{2T_h}$$

Similarly,

$$\Delta S_c = \int_{T_c}^{T_f} \frac{C_v dT}{T} = C_v \ln \frac{T_h + T_c}{2T_c}$$

$$\Delta S = \Delta S_c + \Delta S_h$$

$$= C_v \ln \left[\frac{(T_h + T_c)^2}{4T_h T_c} \right]$$

Since $T_h > T_c$

$$T_h - T_c > 0 \quad (T_h - T_c)^2 > 0$$

$$T_h^2 + T_c^2 > 4T_h T_c$$

$$(T_h + T_c)^2 > 4T_h T_c$$

$$\frac{(T_h + T_c)^2}{4T_h T_c} > 1$$

$$\ln \left[\frac{(T_h + T_c)^2}{4T_h T_c} \right] > 0$$

Therefore,

$$\Delta S > 0$$

Consider a heat engine (Carnot Engine)

$$\Delta U_{\text{engine}} = W + Q_{\text{rev},h} + Q_{\text{rev},c}$$

↑
work done
↑
heat taken
from hot
reservoir
↑
heat
transferred
to cold
reservoir

$$\Delta S_{\text{engine}} = \frac{\delta Q_{\text{rev},h}}{T_h} + \frac{\delta Q_{\text{rev},c}}{T_c}$$

Since the Carnot engine works reversibly

$$\Delta U_{\text{engine}} = 0 \quad W = -Q_{\text{rev},h} - Q_{\text{rev},c}$$

$$\begin{aligned}
 \Delta S_{\text{engine}} &= 0 & \frac{q_{\text{rev},h}}{T_h} &= - \frac{q_{\text{rev},c}}{T_c} \\
 \text{Maximum efficiency} &= \frac{-W}{q_{\text{rev},h}} \\
 (\epsilon) &= \frac{q_{\text{rev},h} + q_{\text{rev},c}}{q_{\text{rev},h}} \\
 &= 1 + \frac{q_{\text{rev},c}}{q_{\text{rev},h}} \\
 &= 1 - \frac{T_c}{T_h} \cdot \frac{q_{\text{rev},h}}{q_{\text{rev},h}} \\
 \epsilon &= 1 - \frac{T_c}{T_h}
 \end{aligned}$$

$$\text{When } T_c = T_h \quad \epsilon = 0$$

Kelvin-Planck Statement
of the 2nd Law of
Thermodynamics

A closed system working in an isothermal cycle cannot convert heat into work without a change in the surroundings.

It is impossible to design a device that works on a cycle that produces no other effect than heat transfer from a single body to produce work.

Clausius Statement

It is impossible to design a device that works on a cycle that produces no effect than to transfer heat from a cold body to a hot body.

PROBLEMS

- (1) Given that C_p is independent of temperature, show that the entropy change (ΔS) for a constant pressure process is

$$\Delta S = C_p \ln \left(\frac{T_2}{T_1} \right)$$

Where T_1 and T_2 are the initial and final temperatures, respectively.

Recall $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$\Delta H \rightarrow$ heat change at constant pressure

$$dH = \delta q_p = C_p dT$$

$$\frac{dH}{T} = \frac{\delta q_p}{T} = \frac{C_p dT}{T}$$

Thus,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

Since C_p is independent of T ,

$$\begin{aligned}\Delta S &= C_p \int_{T_1}^{T_2} \frac{dT}{T} \\ &= C_p \ln\left(\frac{T_2}{T_1}\right)\end{aligned}$$

(2) Show that $\Delta S \geq \frac{q}{T}$. Can $\Delta S < 0$ in a reversible, isothermal process?

From the Clausius inequality,

$$ds \geq \frac{\delta q_r}{T}$$

For an isothermal process

$$\Delta S \geq \int \frac{\delta q_r}{T} \geq \frac{\Delta q_r}{T}$$

Since $T > 0$, the sign of ΔS depends on the sign of Δq_r

$$\Delta S > 0 \quad \text{when} \quad \Delta q_r > 0$$

$$\Delta S < 0 \quad \text{when} \quad \Delta q_r < 0$$

Thus, ΔS can > 0 or < 0 .

Entropy increases with an increase in temperature

$$\begin{aligned}dU &= \delta q_{\text{rev}} - \delta w_{\text{rev}} \\ &= Tds - PdV\end{aligned}$$

Writing $U = f(V, T)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Thus,

$$\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = Tds - PdV$$

$$\begin{aligned}ds &= \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T dV + \frac{P}{T} dV \\ &\quad + \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT\end{aligned}$$

Now,

$$S = f(V, T)$$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

Comparing co-efficients

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V(T)}{T}$$

At constant volume,

$$dS = \frac{C_V(T)}{T}$$

Integrating,

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

$C_V(T) > 0$ so $S_2 - S_1 > 0$ if $T_2 > T_1$

Consider another scenario

$$\begin{aligned}dH &= d(U + PV) \\&= dU + PdV + VdP \\&= Tds - PdV + PdV + VdP \\&= Tds + VdP\end{aligned}$$

Now,

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\begin{aligned}ds &= \frac{1}{T} \left(\frac{\partial H}{\partial P}\right)_T dP - \frac{V}{T} dP \\&\quad + \left(\frac{\partial H}{\partial T}\right)_P dT \\&= \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right] dP + \left(\frac{\partial H}{\partial T}\right)_P dT\end{aligned}$$

Writing $S = f(P, T)$

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT$$

Comparing co-efficients as before

$$\left(\frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right]$$

$$\begin{aligned} \left(\frac{\partial S}{\partial T} \right)_P &= \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P \\ &= \frac{C_p(T)}{T} \end{aligned}$$

At constant pressure

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$

Since $C_p(T) > 0$, $S_2 > S_1$ if $T_2 > T_1$

Entropy always increases with an increase in temperature.

Extra Problems

Take $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. All gases are ideal.

(1) 2.00 mol of an ideal gas at 298 K expands isothermally from $V_1 = 10.0 \text{ L}$ to $V_2 = 25.0 \text{ L}$.

(a) Calculate ΔS_{sys} .

(b) For a reversible expansion, calculate q_{rev} , ΔS_{surr} and ΔS_{total} .

(c) Repeat for an irreversible expansion into vacuum between the same initial and final states.

(a) S is a state function $\rightarrow$ use a reversible isothermal path. For an ideal gas $dU = 0$, so

$$\delta q_{\text{rev}} = -\delta w_{\text{rev}} = \frac{nRT}{V} dV$$

$$\Delta S_{\text{sys}} = \int_1^2 \frac{\delta q_{\text{rev}}}{T} = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$= (2.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{25.0 \text{ L}}{10.0 \text{ L}}\right)$$

$$= 15.2 \text{ J K}^{-1}$$

(b) Heat absorbed along the reversible path:

$$\begin{aligned} q_{\text{rev}} &= T \Delta S_{\text{sys}} \\ &= (298 \text{ K})(15.24 \text{ J K}^{-1}) \\ &= 4.54 \text{ kJ} \end{aligned}$$

This heat is taken reversibly from the surroundings at the same T

$$\Delta S_{\text{surr}} = -\frac{q_{\text{rev}}}{T} = -15.2 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

(c) Same initial and final states, so

$$\Delta S_{\text{sys}} = +15.2 \text{ J K}^{-1}$$

Expansion into vacuum: $w = 0$ and $\Delta U = 0$ (T is constant), so $q = 0$. The surroundings do not change.

$$\Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{total}} = 15.2 \text{ J K}^{-1} + 0 > 0$$

ΔS_{sys} is the same in (b) and (c). Only ΔS_{surr} , and so ΔS_{total} , is different.

(2) 3.00 mol of N_2 and 1.00 mol of O_2 , both at 298 K and 1.00 bar, are in two compartments separated by a partition. The partition is removed and the gases mix isothermally.

(a) Calculate the mole fraction of each gas.

(b) Calculate the molar entropy of mixing, $\overline{\Delta S}$.

(c) Calculate the total entropy of mixing, ΔS .

(d) Calculate ΔS_{N_2} and ΔS_{O_2} and show that they add up to the answer in (c).

$$(a) N = n_{N_2} + n_{O_2} = 4.00 \text{ mol}$$

$$x_{N_2} = \frac{3.00}{4.00} = 0.750$$

$$x_{O_2} = \frac{1.00}{4.00} = 0.250$$

Both gases start at the same T and P , so volume fraction = mole fraction

$$\frac{V_A}{V_A + V_B} = x_A$$

(b) Molar entropy of mixing:

$$\overline{\Delta S} = -R \sum_i x_i \ln x_i$$

$$= -R [0.750 \ln 0.750 + 0.250 \ln 0.250]$$

$$= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(-0.5623)$$

$$= 4.68 \text{ J K}^{-1} \text{ mol}^{-1}$$

(c) Multiply by the total number of moles:

$$\begin{aligned}\Delta S &= N \overline{\Delta S} \\ &= (4.00 \text{ mol})(4.675 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 18.7 \text{ J K}^{-1}\end{aligned}$$

(d) Each gas expands isothermally into the full volume

$$\Delta S_i = -n_i R \ln x_i$$

$$\begin{aligned}\Delta S_{N_2} &= - (3.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 0.750 \\ &= 7.18 \text{ J K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S_{O_2} &= - (1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 0.250 \\ &= 11.5 \text{ J K}^{-1}\end{aligned}$$

$$7.175 + 11.526 = 18.70 \text{ J K}^{-1} \quad \checkmark$$

O_2 expands 4-fold but N_2 only by 4/3, so O_2 contributes more even though there is less of it.

(3) Two identical blocks, each with $C_V = 385 \text{ J K}^{-1}$ (independent of T), are at $T_h = 400 \text{ K}$ and $T_c = 300 \text{ K}$. They are brought into thermal contact in an insulated container. No work is done.

(a) Calculate the final temperature T_f .

(b) Calculate ΔS_h for the hot block.

(c) Calculate ΔS_c for the cold block.

(d) Calculate the total ΔS and check it against the formula in the notes.

(a) Isolated and no work, so the energy lost by the hot block is gained by the cold block

$$C_V (T_f - T_h) + C_V (T_f - T_c) = 0$$

$$T_f = \frac{T_h + T_c}{2} = \frac{400 \text{ K} + 300 \text{ K}}{2} = 350 \text{ K}$$

(b) The heat flow is irreversible, but ΔS is found over a reversible path with $\delta q_{\text{rev}} = C_V dT$

$$\begin{aligned}\Delta S_h &= \int_{T_h}^{T_f} \frac{C_V dT}{T} = C_V \ln\left(\frac{T_f}{T_h}\right) \\ &= (385 \text{ J K}^{-1}) \ln\left(\frac{350 \text{ K}}{400 \text{ K}}\right) \\ &= -51.4 \text{ J K}^{-1}\end{aligned}$$

(c) Similarly,

$$\begin{aligned}\Delta S_c &= C_v \ln\left(\frac{T_f}{T_c}\right) \\ &= (385 \text{ J K}^{-1}) \ln\left(\frac{350 \text{ K}}{300 \text{ K}}\right) \\ &= +59.3 \text{ J K}^{-1}\end{aligned}$$

(d) Small difference of two larger numbers $\rightarrow$ keep an extra digit

$$\begin{aligned}\Delta S &= \Delta S_h + \Delta S_c \\ &= -51.41 \text{ J K}^{-1} + 59.35 \text{ J K}^{-1} \\ &= +7.94 \text{ J K}^{-1}\end{aligned}$$

Check with the formula from the notes:

$$\begin{aligned}\Delta S &= C_v \ln\left[\frac{(T_h + T_c)^2}{4 T_h T_c}\right] \\ &= (385 \text{ J K}^{-1}) \ln\left[\frac{(700 \text{ K})^2}{4 (400 \text{ K})(300 \text{ K})}\right] \\ &= (385 \text{ J K}^{-1}) \ln(1.0208) \\ &= 7.94 \text{ J K}^{-1} \quad \checkmark\end{aligned}$$

$\Delta S > 0$, as expected for a spontaneous process in an isolated system.