Physical Chemistry for Energy Engineering

(7rh: 2018/10/1)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (tentative)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Thermodynamics: The second and third laws of thermodynamics-3 (1. Equation of state of gas will be covered in future)
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	

(Review) 1.3.1. The 2nd law of thermodynamics

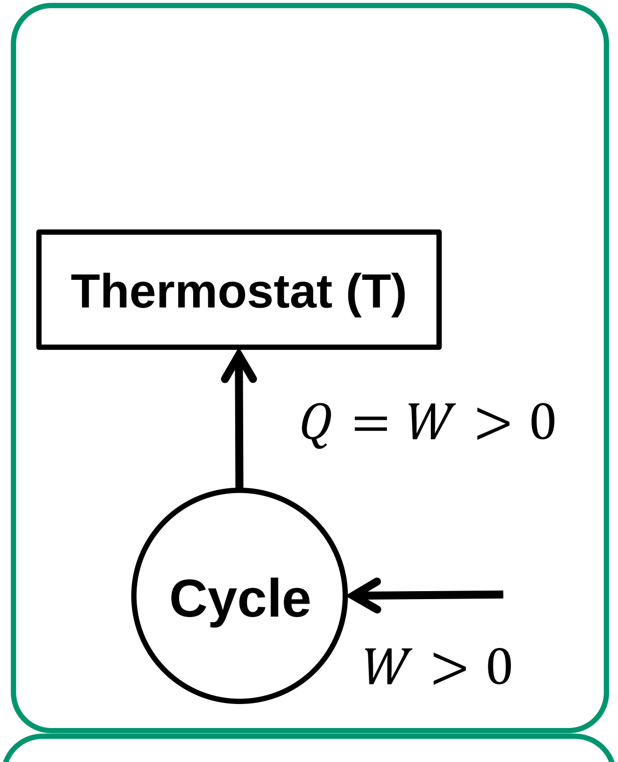
- description-

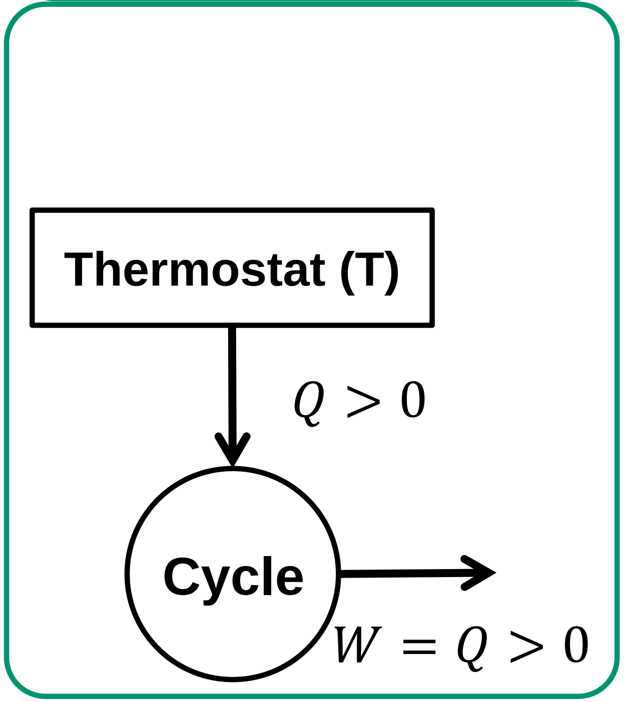
- ✓ *"The entropy of an isolated system never decreases, because isolated systems always evolve toward thermodynamic equilibrium—the state with the maximum possible entropy." (wikipedia)*

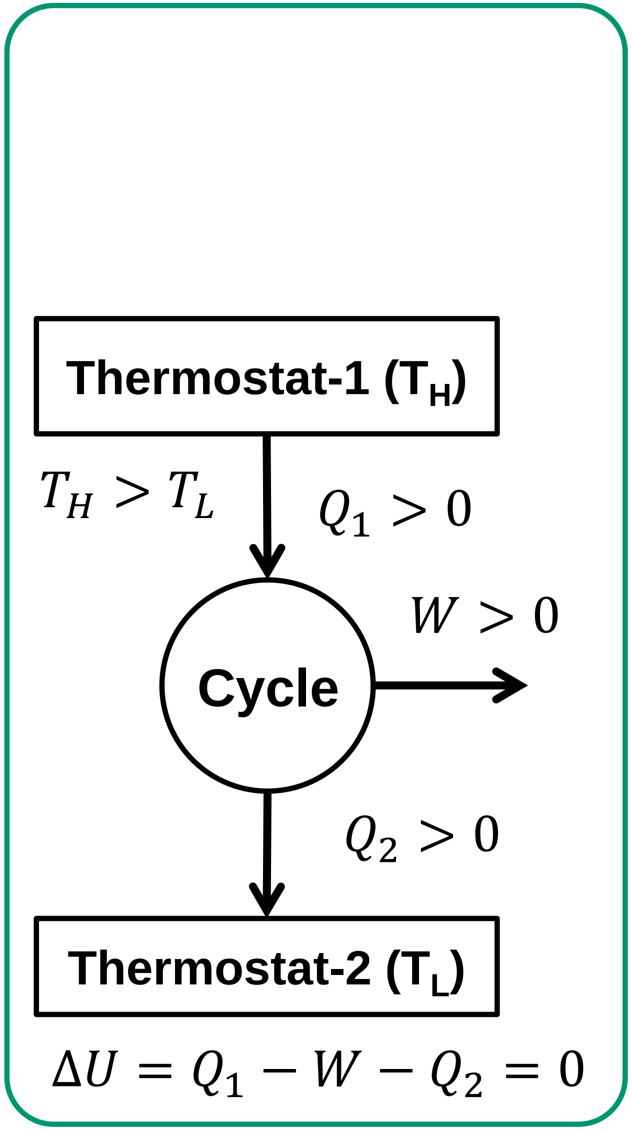
- ✓ *"Heat cannot spontaneously flow from cold regions to hot regions without external work being performed on the system." (Clausius statement)*

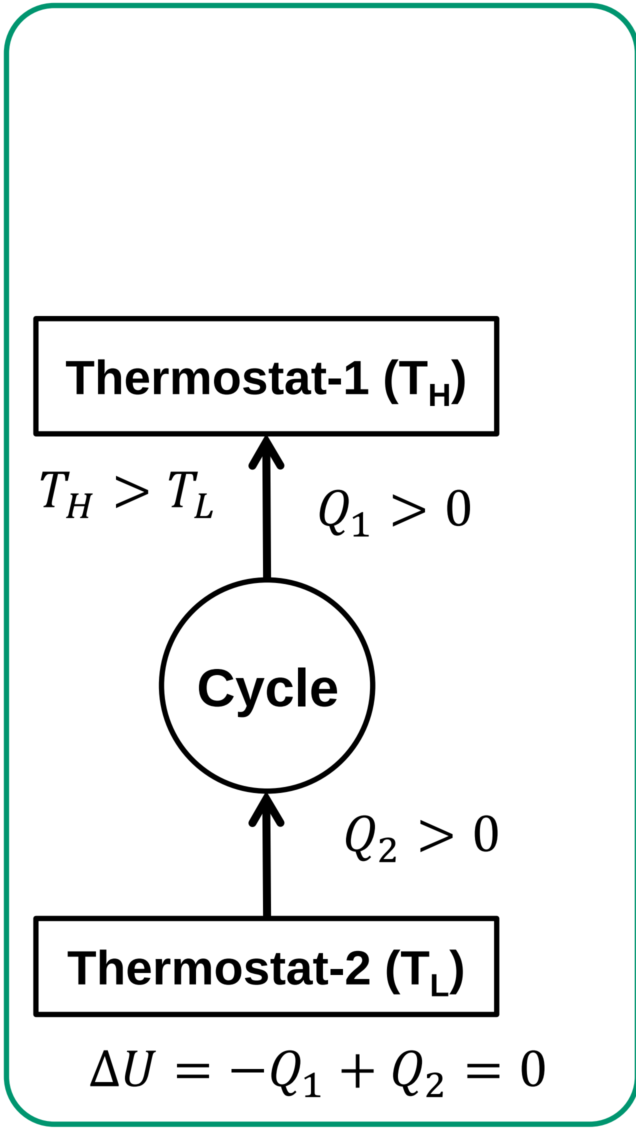
- ✓ *"The efficiency of a quasi-static or reversible Carnot cycle depends only on the temperatures of the two heat reservoirs, and is independent of the working substance. A Carnot engine operated in this way is the most efficient possible heat engine using those two temperatures." (Carnot's principle)*

- ✓ *"There is no thermodynamic cycle that can absorb energy (>0) from a sole thermostat and then convert all the absorbed energy to a work to the surroundings." (Thomson's statement)*

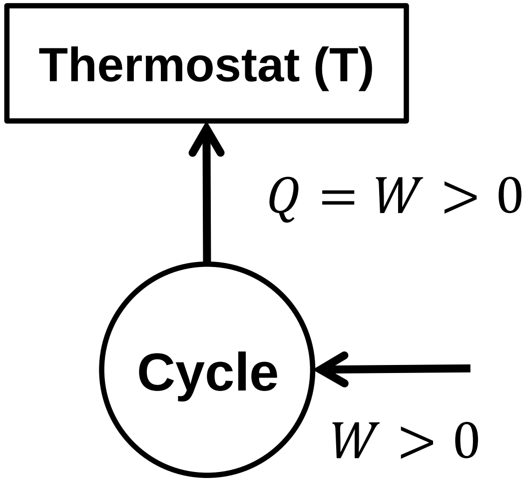

Thermostat (T)
$Q = W > 0$
Cycle
$W > 0$


Thermostat (T)
$Q > 0$
Cycle
$W = Q > 0$

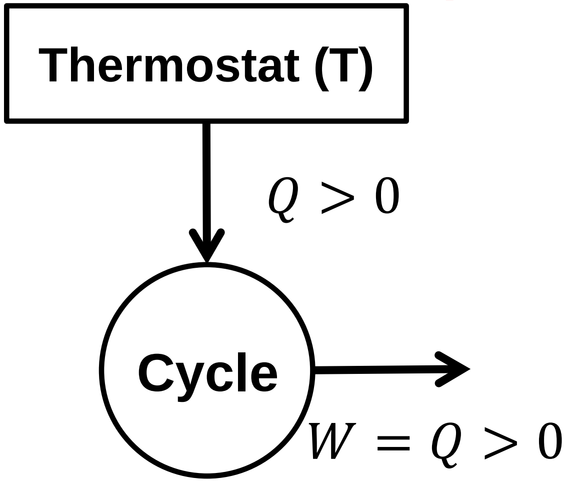

Thermostat-1 (T_H)
$T_H > T_L$
$Q_1 > 0$
$W > 0$
Cycle
$Q_2 > 0$
Thermostat-2 (T_L)
$\Delta U = Q_1 - W - Q_2 = 0$


Thermostat-1 (T_H)
$T_H > T_L$
$Q_1 > 0$
Cycle
$Q_2 > 0$
Thermostat-2 (T_L)
$\Delta U = -Q_1 + Q_2 = 0$

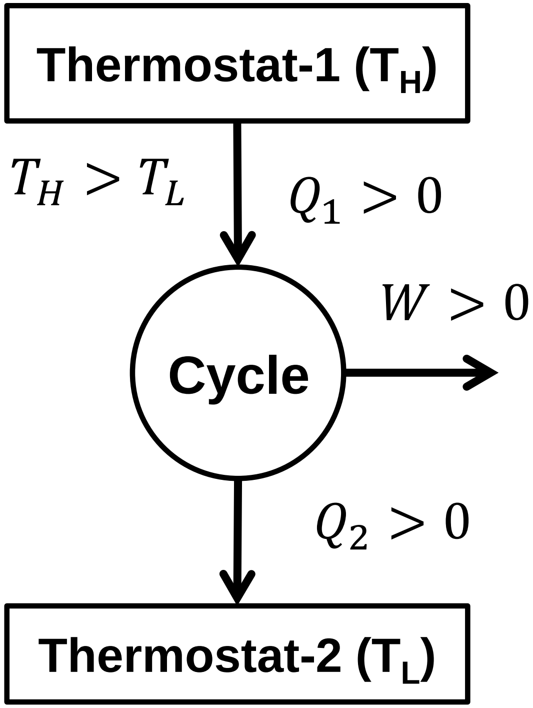
Feasible
(full conversion of work to heat)



Unfeasible
(full conversion of heat to work)

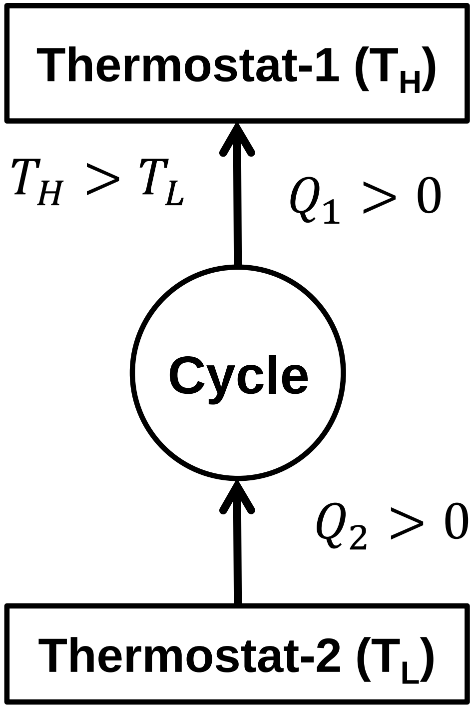


Feasible
(e.g. normal engine)



$$\Delta U = Q_1 - W - Q_2 = 0$$

Unfeasible
(energy flow as heat from low-T to high-T with no work input)



$$\Delta U = -Q_1 + Q_2 = 0$$

(Review) 1.3.1. The 2nd law of thermodynamics
- Definition of entropy -

The efficiency (η) of a general cycle (engine) can be defined as

$$\eta = \frac{W_{out}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

For Carnot cycle, the efficiency is rewritten as

$$\eta_C = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_L}{T_H}$$

The efficiency of a (general) cycle <u>using 2 thermostats </u>is less than the efficiency of Carnot cycle.

$$\eta \le \eta_c = 1 - \frac{T_L}{T_H} \qquad \left(\eta = 1 - \frac{Q_2}{Q_1}\right)$$

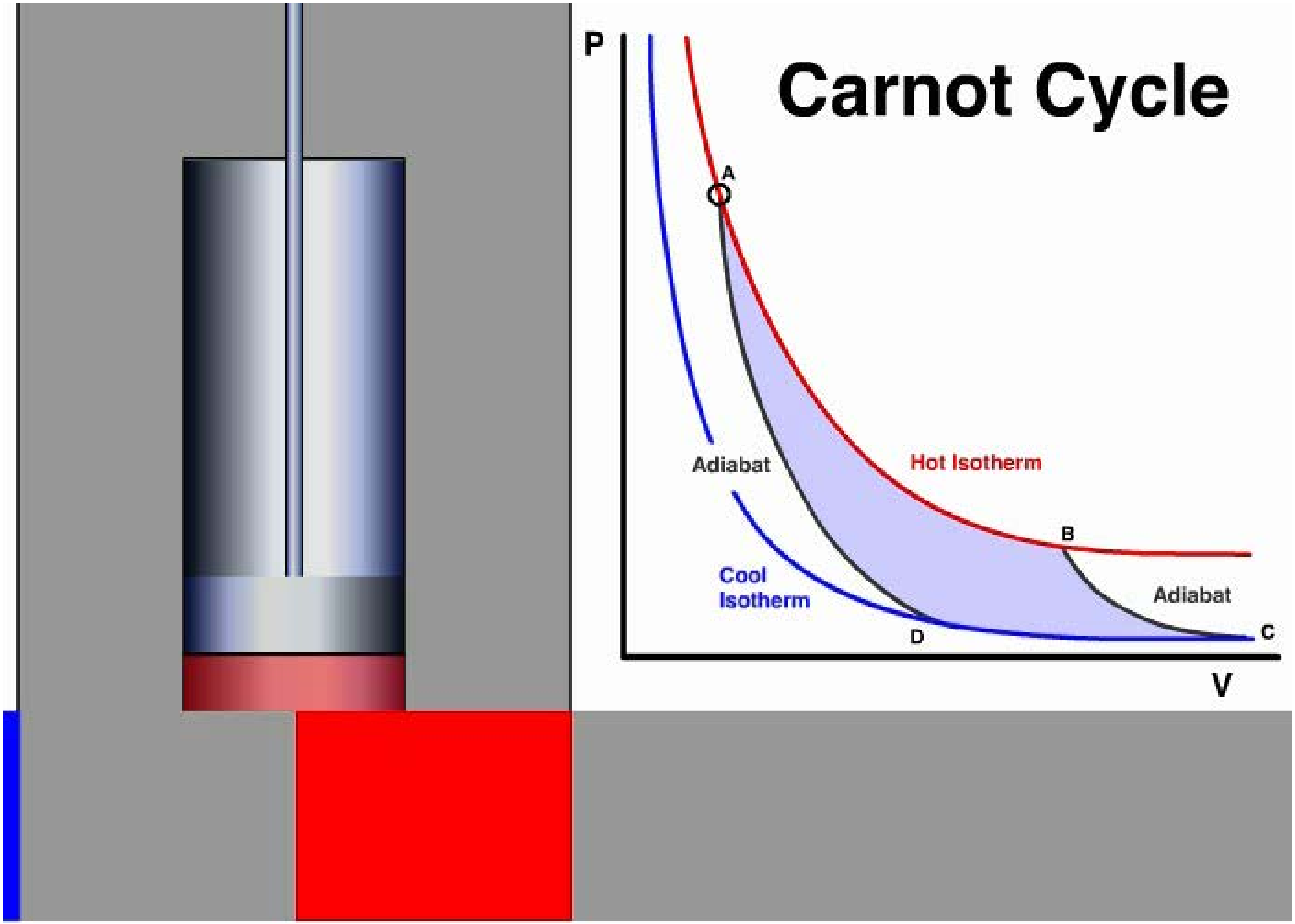
The equal sign is achieved when the cycle is reversible.

We derived the following equation which is applicable for any cycle in a closed system, based on the 2nd law statement:

$$\oint \frac{\delta q}{T} \le 0$$

where equal sign is for reversible process and the unequal is for irreversible.

(Review) 1.3.1. The 2nd law of thermodynamics
- Carnot cycle -



http://science.sbcc.edu/~physics/flash/heatengines/Carnot%20cycle.html

(Review) 1.3.1. The 2nd law of thermodynamics
- Comparison with other statements -

<another important statement of the Second Law of Thermodynamics>
There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the system,

$$dS \geq \frac{\delta q}{T}$$

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.

(Appendix) The 1st law equation for reversible processes

(Question) Is it OK that $\frac{\delta q_{rev}}{T}$ is of a state function while δq is of a path function?

- ✓ This is similar to $dU = \delta q + \delta w$, where the left side is of a state function while the right side is of path functions.
- ✓ In addition, $\delta w_{rev} = -PdV$ is also a similar condition.

Here, we reconsider the form of 1st law.

- ✓ The general format of the 1st law is always correct (either reversible or irreversible process):

$$dU = \delta q + \delta w$$

- ✓ If we only consider P-V work and consider the process is reversible, then:

$$\delta w_{rev} = -P_{ext}dV = -PdV$$

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

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

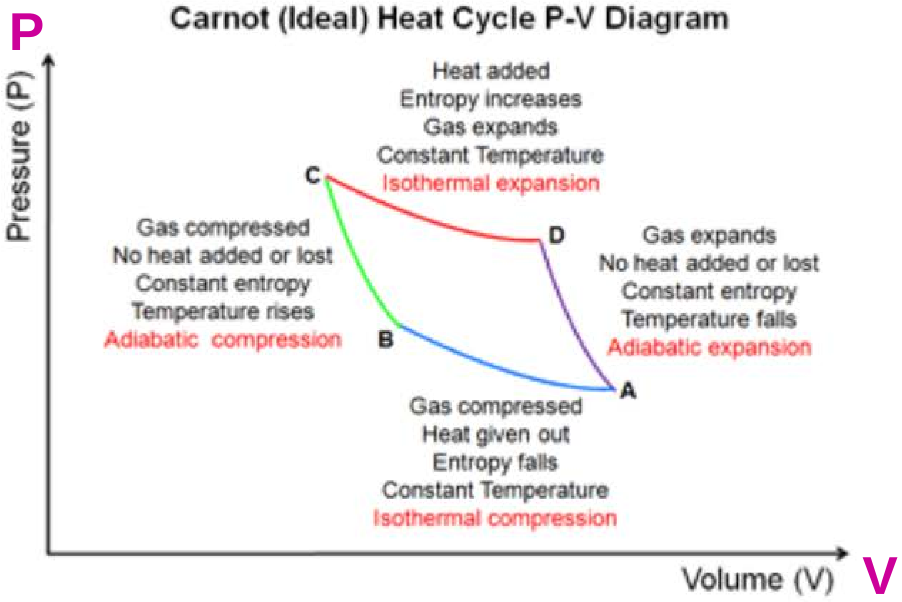
$dU = TdS - PdV$ (for reversible process)

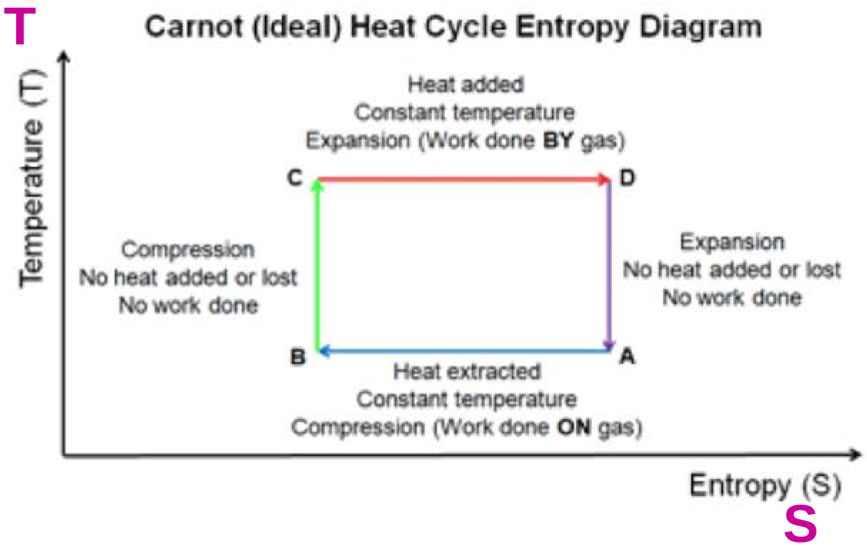
**Indeed, this equation is also correct for some irreversible processes as far as these thermodynamic quantities are definable throughout the process. This is because there quantities are state functions.*

V-P and S-T diagrams

$dU = TdS - PdV$ [derivative], $\Delta U = \int TdS - \int PdV$ [integral] (reversible proc.)

For reversible processes, the area surrounded by a circle (clockwise) in V-P diagram corresponds to the energy transferred from the system to the surroundings as work, while that in S-T diagram corresponds to the energy transferred from the surroundings to the system as heat.





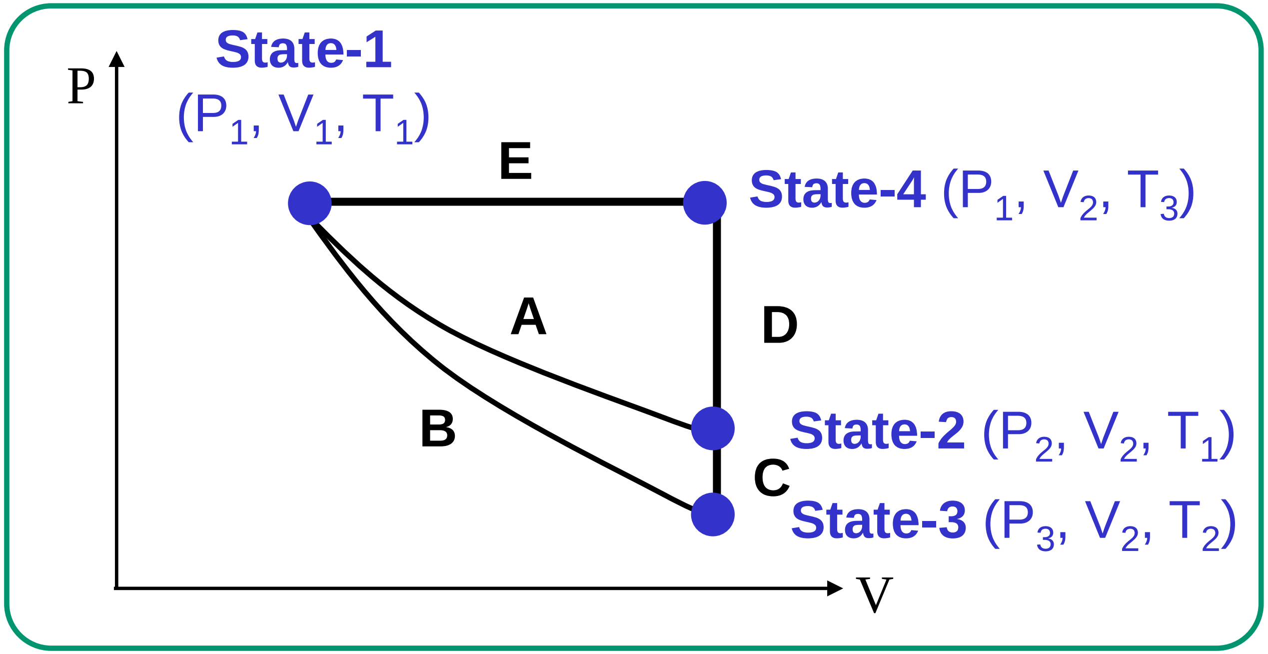
*If you have time, please check V-P and S-T diagrams for several typical cycles in : http://www.mpoweruk.com/heat_engines.htm

1.3.1. The 2nd law of thermodynamics

- entropy in a thermodynamic cycle: exercise -

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $\mathrm{w},$ for each process.

- ✓ [Path-A] Reversible isothermal expansion: s-1 (P_1, V_1, T_1)→ s-2 (P_2, V_2, T_1)
- ✓ [Path-B] Reversible adiabatic expansion: s-1 (P_1, V_1, T_1) → s-3 (P_3, V_2, T_2)
- ✓ [Path-C] Reversible constant-V heating: s-3 (P_3, V_2, T_2) → s-2(P_2, V_2, T_1)
- ✓ [Path-D] Reversible constant-V heating: s-2 (P_2, V_2, T_1) → s-4 (P_1, V_2, T_3)
- ✓ [Path-E] Reversible constant-P cooling: s-4 (P_1, V_2, T_3) → s-1 (P_1, V_1, T_1)

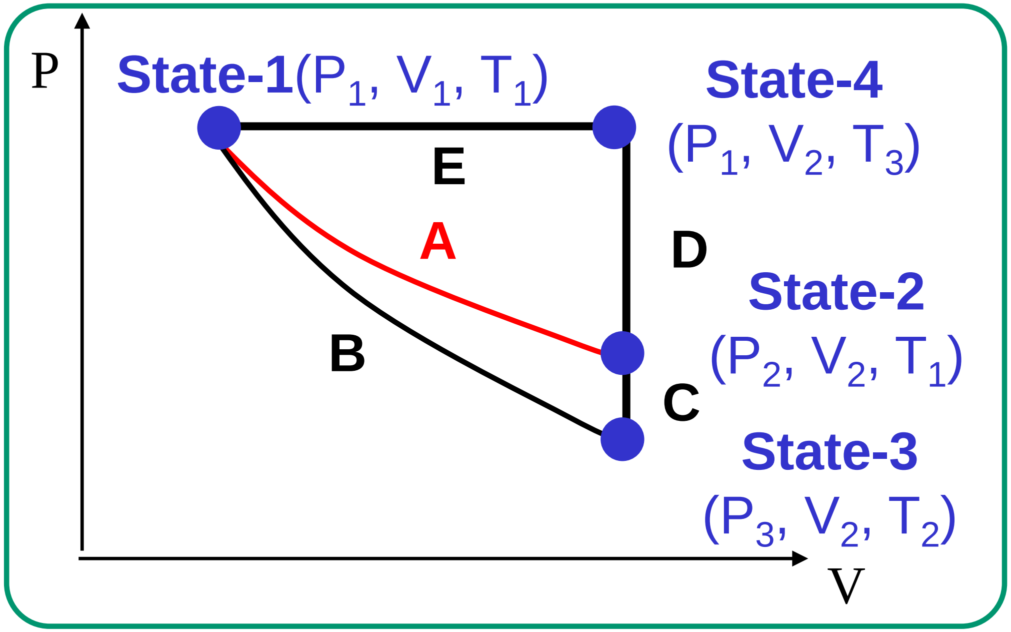


1st law: [derivative form] $\mathrm{d}U = \delta q + \delta w$; [integral form] $\Delta U = q + w$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (path-A)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $w,$ for each process.

[Path-A] Reversible isothermal expansion:
s-1 $(P_1, V_1, T_1) \rightarrow$
s-2 (P_2, V_2, T_1)

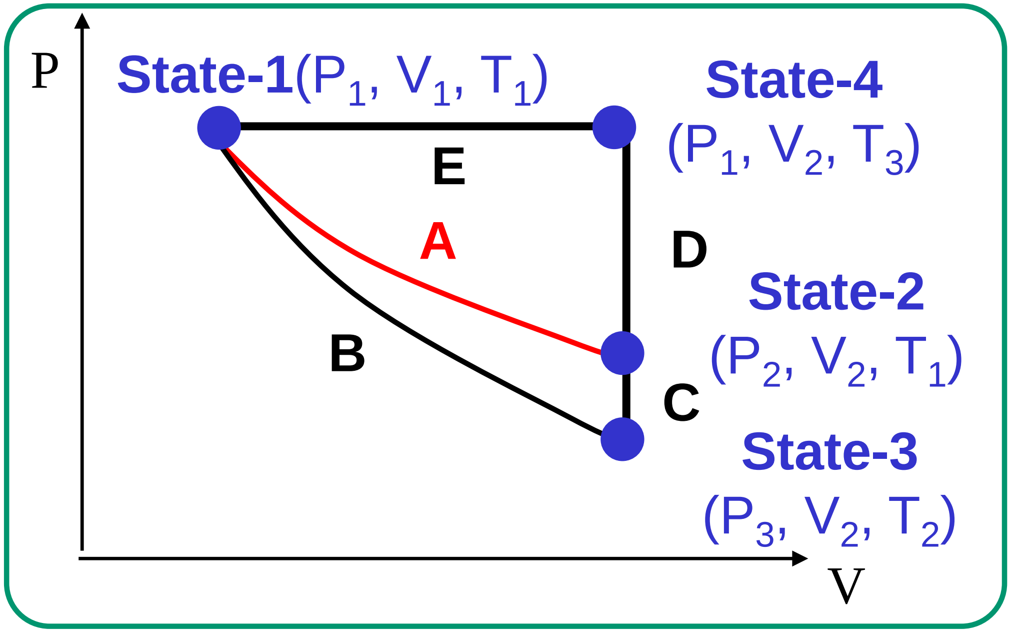


$\Delta U_A = 0$
$q_A = nRT_1 \times \ln \frac{V_2}{V_1}$
$w_A = -nRT_1 \times \ln \frac{V_2}{V_1}$
$\Delta S_A =$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (path-A)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $\mathrm{w},$ for each process.

[Path-A] Reversible isothermal expansion:
s-1 (P_1, V_1, T_1)→
s-2 (P_2, V_2, T_1)



As the energy of ideal gas only depends on temperature and $dT = 0$, $dU = 0$.

The first law can be re-written as $\delta q_A = -\delta w_A$, then

$$\Delta S_A = \int_{s-1}^{s-2} \frac{\delta q_{A,rev}}{T} = -\int_{s-1}^{s-2} \frac{\delta w_{A,rev}}{T} = \int_{V_2}^{V_2} \frac{P}{T} dV$$

$$= nR \int_{V_2}^{V_2} \frac{dV}{V} = nR \times \ln \frac{V_2}{V_1}$$

*In this case, as $T = const.$ you can also simply estimate as $\Delta S_A = \int_{s-1}^{s-2} \frac{\delta q_{A,rev}}{T} = \frac{1}{T_1} \int_{s-1}^{s-2} \delta q_{A,rev} = \frac{q_A}{T_1}$

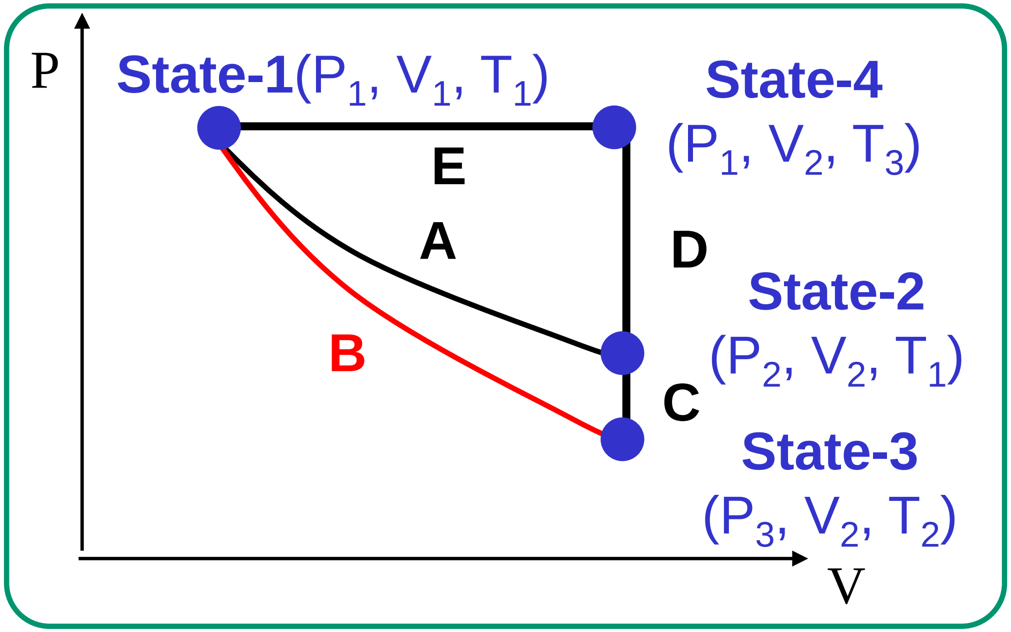
$\Delta U_A = 0$
$q_A = nRT_1 \times \ln \frac{V_2}{V_1}$
$w_A = -nRT_1 \times \ln \frac{V_2}{V_1}$
$\Delta S_A = nR \times \ln \frac{V_2}{V_1}$

1.3.1. The 2nd law of thermodynamics

- entropy in a thermodynamic cycle: exercise (path-B)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $dU = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $w,$ for each process.

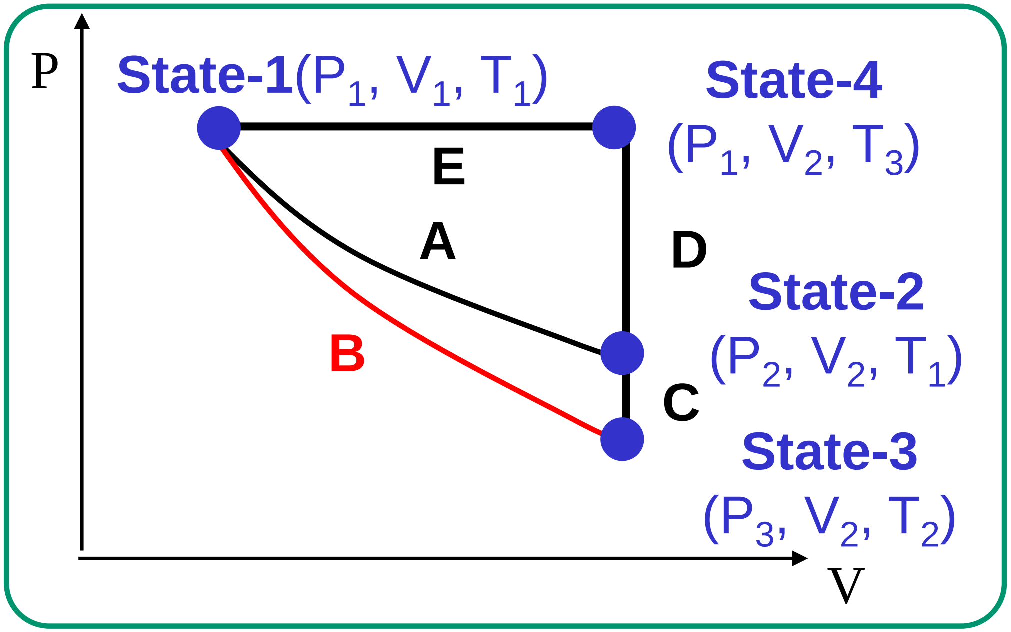
[Path-B] Reversible adiabatic expansion:
s-1 (P_1, V_1, T_1) → s-3 (P_3, V_2, T_2)



$\Delta U_B = C_V(T_2 - T_1)$
$q_B = 0$
$w_B = C_V(T_2 - T_1)$
$\Delta S_B =$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (path-B)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $\mathrm{w},$ for each process.



[Path-B] Reversible adiabatic expansion:
s-1 (P_1, V_1, T_1) →
s-3 (P_3, V_2, T_2)

As adiabatic process ($\delta q = 0$):

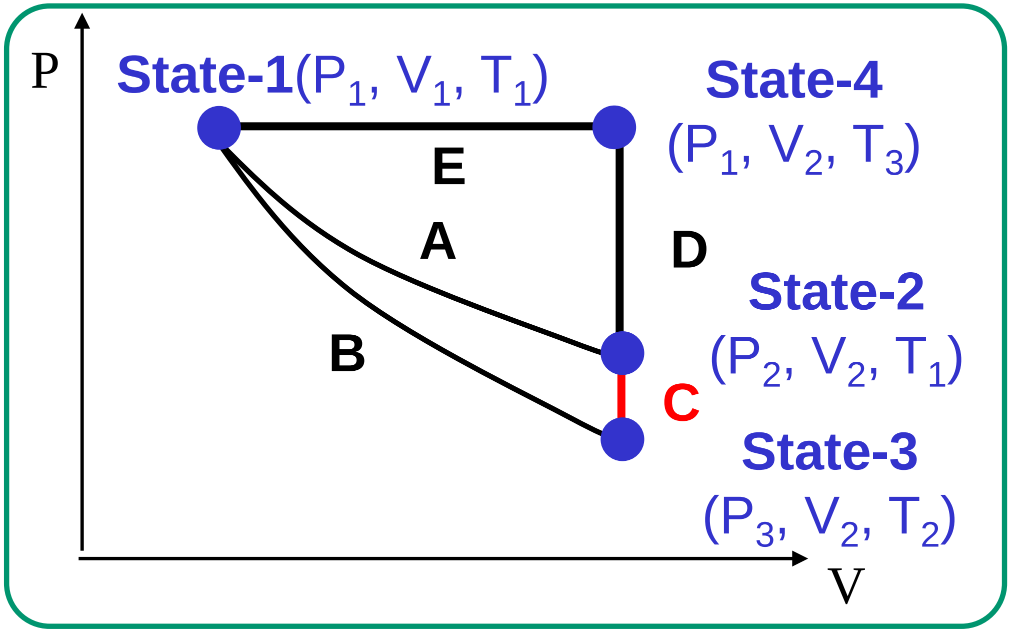
$$\Delta S_B = \int_{s-1}^{s-3} \frac{\delta q_{B,rev}}{T} = 0$$

$\Delta U_B = C_V(T_2 - T_1)$
$q_B = 0$
$w_B = C_V(T_2 - T_1)$
$\Delta S_B = 0$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (path-C)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $\mathrm{w},$ for each process.

[Path-C] Reversible constant-V heating:
s-3 (P_3, V_2, T_2) → s-2(P_2, V_2, T_1)



$$\Delta U_C = C_V(T_1 - T_2)$$

$$q_C = C_V(T_1 - T_2)$$

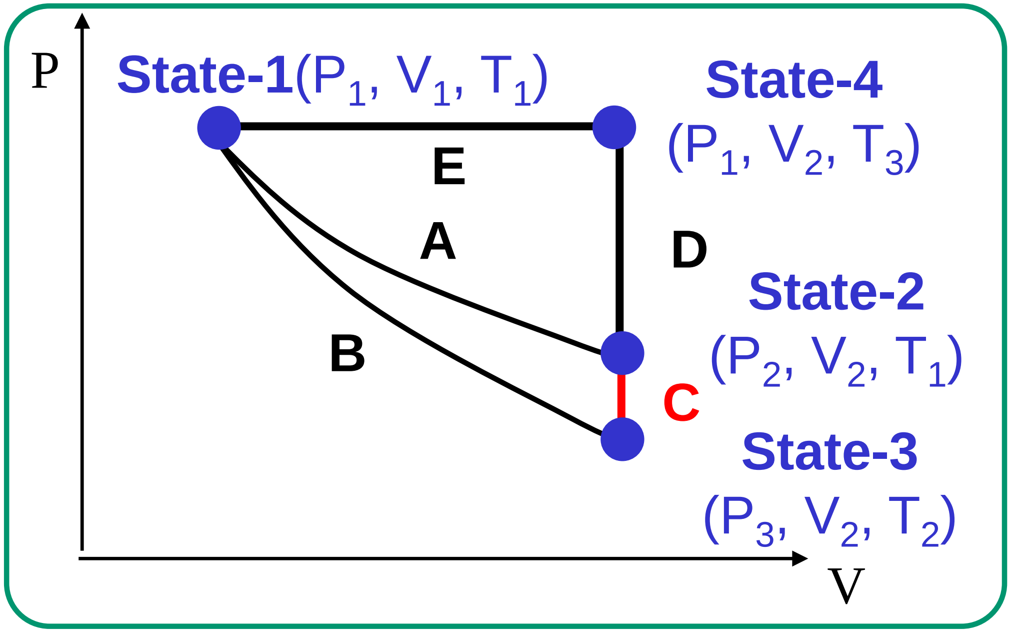
$$w_C = 0$$

$\Delta S_C =$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (path-C)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) ΔU, (2) q, (3) w, for each process.

[Path-C] Reversible constant-V heating:
s-3 (P_3, V_2, T_2) → s-2(P_2, V_2, T_1)



As constant-V process ($dV = 0$), $\delta w_C = -P_{ext} dV = 0$.

Then, the first law is: $dU_C = \delta q_C$

As we assume the system is of an ideal gas ($dU = C_V dT$):

$$\Delta S_C = \int_{s-3}^{s-2} \frac{\delta q_{C,rev}}{T} = \int_{s-3}^{s-2} \frac{dU}{T} = C_V \int_{s-3}^{s-2} \frac{dT}{T}$$

$$= C_V \times \ln \frac{T_1}{T_2}$$

$$\Delta U_C = C_V (T_1 - T_2)$$

$$q_c = C_V (T_1 - T_2)$$

$$w_c = 0$$

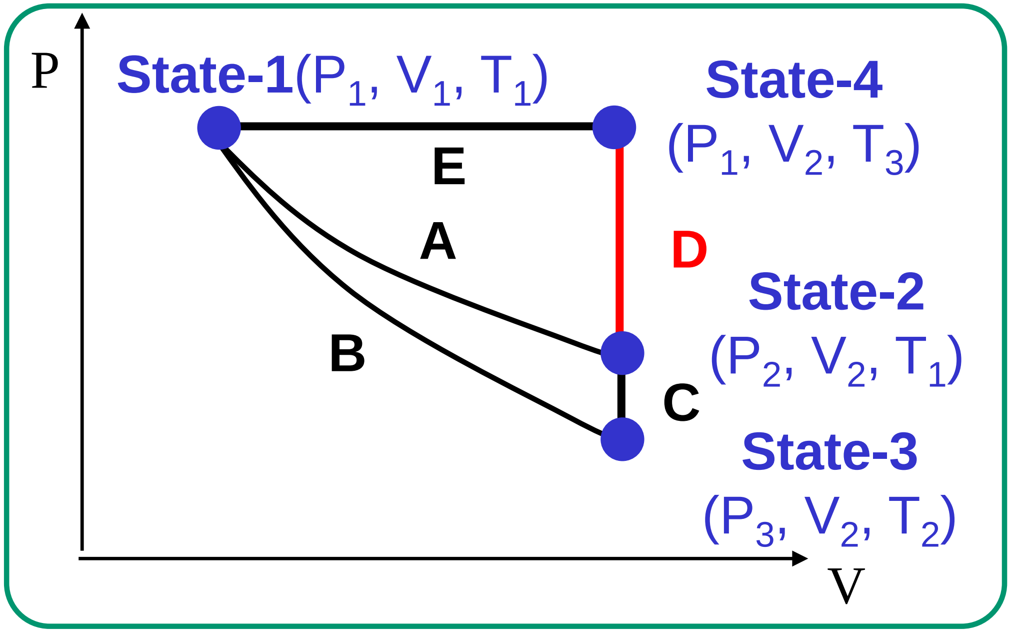
$$\Delta S_C = C_V \times \ln \frac{T_1}{T_2}$$

1.3.1. The 2nd law of thermodynamics

- entropy in a thermodynamic cycle: exercise (path-D)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $w,$ for each process.

[Path-D] Reversible constant-V heating:
s-2 (P_2, V_2, T_1) → s-4 (P_1, V_2, T_3)



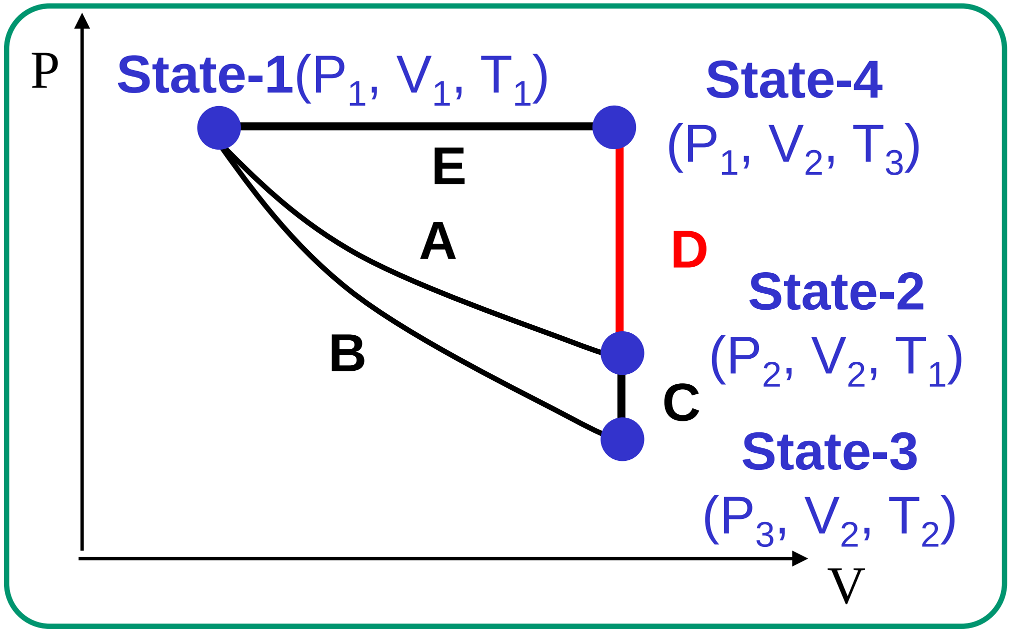
$\Delta U_D = C_V(T_3 - T_1)$
$q_D = C_V(T_3 - T_1)$
$w_D = 0$
$\Delta S_D =$

1.3.1. The 2nd law of thermodynamics

- entropy in a thermodynamic cycle: exercise (path-D)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $\mathrm{w},$ for each process.

[Path-D] Reversible constant-V heating:
s-2 (P_2, V_2, T_1) → s-4 (P_1, V_2, T_3)



As constant-V process ($dV = 0$), $\delta w_C = -P_{ext} dV = 0$.

Then, the first law is: $dU_D = \delta q_D$

As we assume the system is of an ideal gas ($dU = C_V dT$):

$$\Delta S_D = \int_{s-2}^{s-4} \frac{\delta q_{D,rev}}{T} = \int_{s-2}^{s-4} \frac{dU}{T} = C_V \int_{s-2}^{s-4} \frac{dT}{T}$$

$$= C_V \times \ln \frac{T_3}{T_1}$$

$$\Delta U_D = C_V(T_3 - T_1)$$

$$q_D = C_V(T_3 - T_1)$$

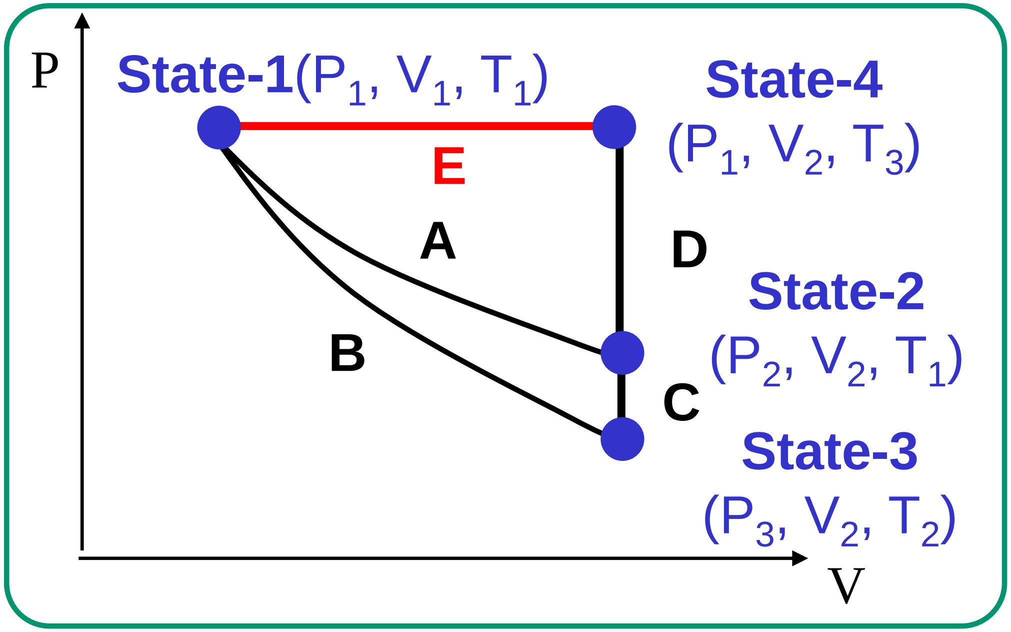
$$w_D = 0$$

$$\Delta S_D = C_V \times \ln \frac{T_3}{T_1}$$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (path-E)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $\mathrm{d}U = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $w,$ for each process.

[Path-E] Reversible constant-P cooling:
s-4 (P_1, V_2, T_3) →
s-1 (P_1, V_1, T_1)



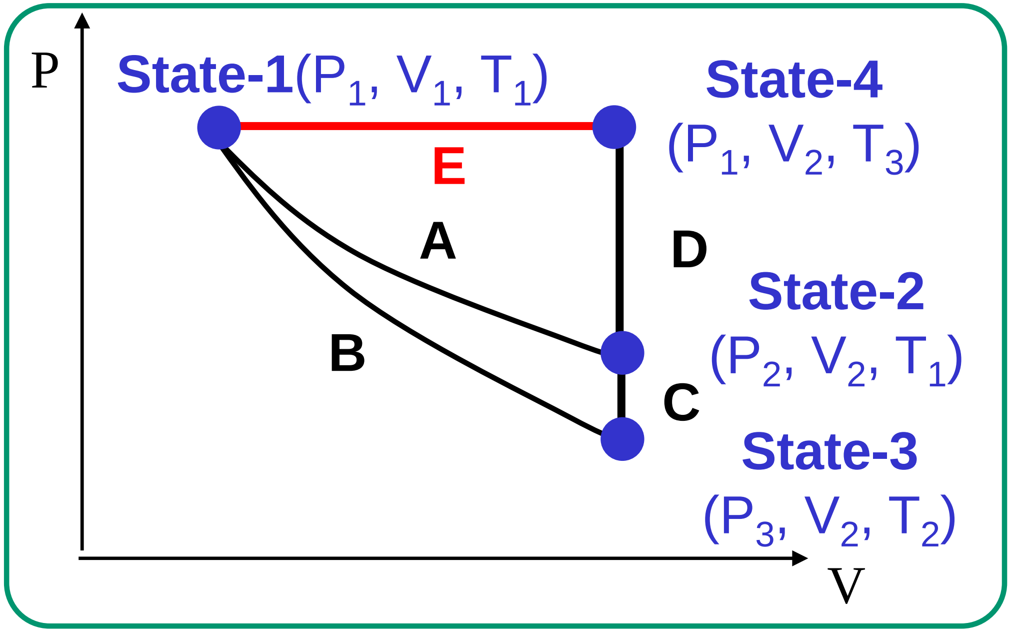
$\Delta U_E = C_V(T_1 - T_3)$
$q_E = C_V(T_1 - T_3) + P_1(V_1 - V_2)$
$w_E = -P_1(V_1 - V_2)$
$\Delta S_E =$

1.3.1. The 2nd law of thermodynamics

- entropy in a thermodynamic cycle: exercise (path-E)-

Assuming n mole of idea gas ($PV = nRT$, $U = U(T)$, $dU = C_V dT$ and $C_V = \alpha nR = const.$), please evaluate (1) $\Delta U,$ (2) $q,$ (3) $w,$ for each process.

[Path-E] Reversible constant-P cooling:
s-4 (P_1, V_2, T_3) → s-1 (P_1, V_1, T_1)



As reversible constant-P process ($P = P_{ext}$ and $dP = 0$),

$$w_E = -\int PdV = -P_1 \int dV = -P_1(V_1 - V_2).$$

As we assume the system is of an ideal gas ($dU = C_V dT$). Then using the first law:

$$\Delta S_E = \int_{s-4}^{s-1} \frac{\delta q_{E,rev}}{T} = \int_{s-4}^{s-1} \frac{dU_E - \delta w_E}{T}$$

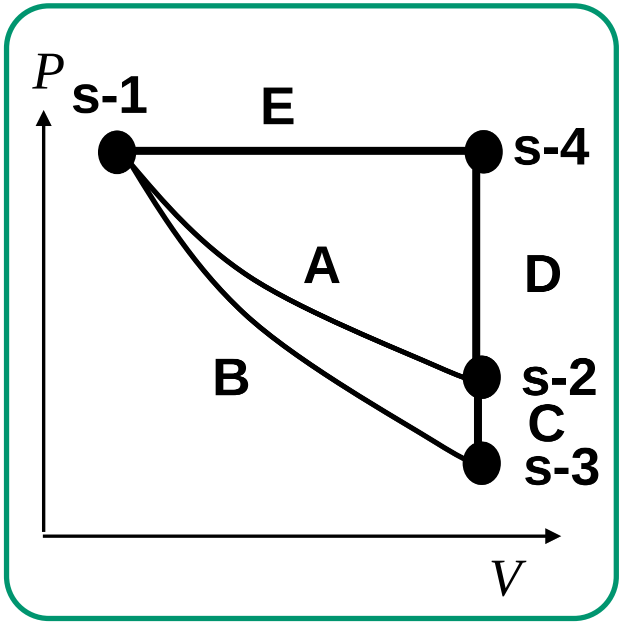
$$= C_V \int_{s-4}^{s-1} \frac{dT}{T} + \int_{s-4}^{s-1} \frac{P}{T} dV = C_V \times \ln\frac{T_1}{T_3} + nR \times \ln\frac{V_1}{V_2}$$

$\Delta U_E = C_V(T_1 - T_3)$
$q_E = C_V(T_1 - T_3) + P_1(V_1 - V_2)$
$w_E = -P_1(V_1 - V_2)$
$\Delta S_E = C_V \times \ln\frac{T_1}{T_3} + nR \times \ln\frac{V_1}{V_2}$

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (summary)-

- ✓ [Path-A] Reversible isothermal expansion: s-1 $(P_1, V_1, T_1) \rightarrow$ s-2 (P_2, V_2, T_1)
- ✓ [Path-B] Reversible adiabatic expansion: s-1 $(P_1, V_1, T_1) \rightarrow$ s-3 (P_3, V_2, T_2)
- ✓ [Path-C] Reversible constant-V heating: s-3 $(P_3, V_2, T_2) \rightarrow$ s-2(P_2, V_2, T_1)
- ✓ [Path-D] Reversible constant-V heating: s-2 $(P_2, V_2, T_1) \rightarrow$ s-4 (P_1, V_2, T_3)
- ✓ [Path-E] Reversible constant-P cooling: s-4 $(P_1, V_2, T_3) \rightarrow$ s-1 (P_1, V_1, T_1)

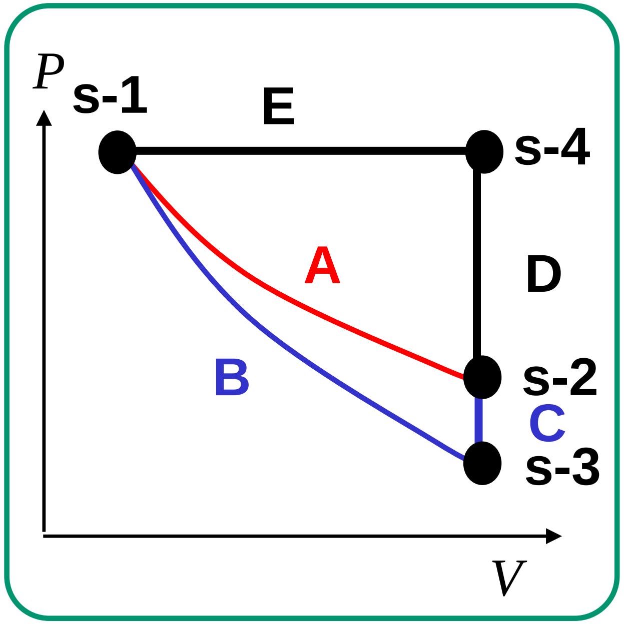
Path	ΔS	q
A	$nR \times \ln \frac{V_2}{V_1}$	$nRT_1 \times \ln \frac{V_2}{V_1}$
B	0	0
C	$C_V \times \ln \frac{T_1}{T_2}$	$C_V(T_1 - T_2)$
D	$C_V \times \ln \frac{T_3}{T_1}$	$C_V(T_3 - T_1)$
E	$C_V \times \ln \frac{T_1}{T_3} + nR \times \ln \frac{V_1}{V_2}$	$C_V(T_1 - T_3)$ $+ P_1(V_1 - V_2)$



✓ ΔS is not equal to $^{q}/_{T}$ if either $dT = 0$ (isothermal) or $\delta q = 0$ (adiabatic) is not kept during the process. The paths C,D ad E are such cases.

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (summary)-

Path	ΔS
A	$nR \times \ln(V_2/V_1)$
B	0
C	$C_V \times \ln(T_1/T_2)$
D	$C_V \times \ln(T_3/T_1)$
E	$C_V \times \ln(T_1/T_3) + nR \times \ln(V_1/V_2)$



(1) [Path-A] v.s. [Path-B+C]

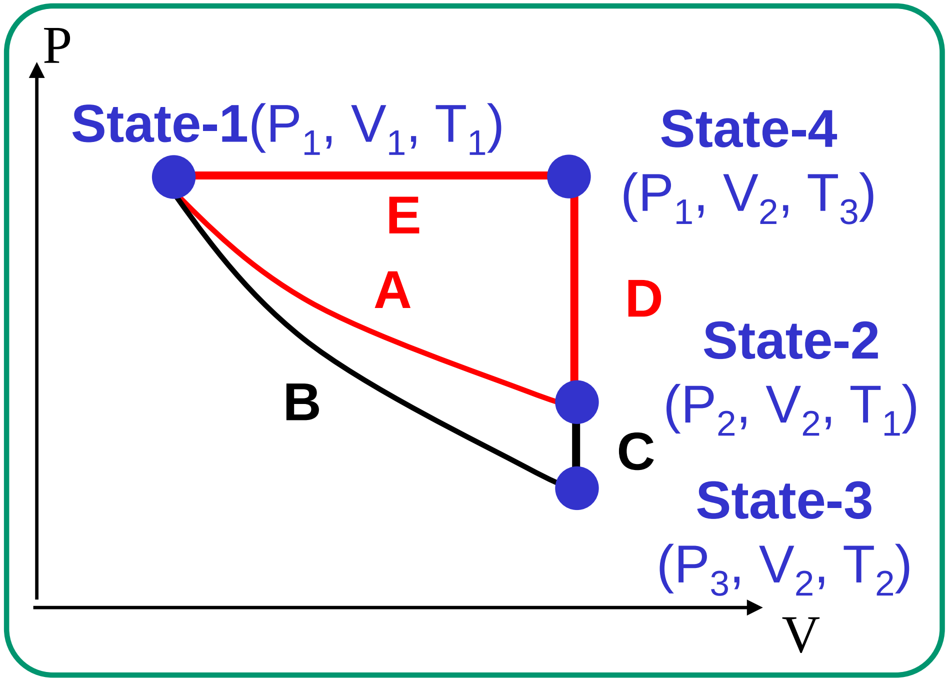
For adiabatic process, $\left(\frac{T_{fin}}{T_{ini}}\right)^{\alpha} = \left(\frac{V_{ini}}{V_{fin}}\right)$ where $\alpha = const.$ and $C_V = \alpha nR$ (e.g. $\alpha = \frac{3}{2}$ for He) for ideal gas. Thus,

$$\Delta S_{B+C} = 0 + C_V \times \ln\frac{T_1}{T_2} = C_V \times \ln\frac{T_1}{T_2} = \alpha nR \times \ln\frac{T_1}{T_2} = nR \times \ln\frac{V_2}{V_1} = \Delta S_A$$

✓ This result is consistent with the fact that S is a state function.

1.3.1. The 2nd law of thermodynamics
- entropy in a thermodynamic cycle: exercise (summary)-

Path	ΔS
A	$nR \times \ln(V_2/V_1)$
B	0
C	$C_V \times \ln(T_1/T_2)$
D	$C_V \times \ln(T_3/T_1)$
E	$C_V \times \ln(T_1/T_3) + nR \times \ln(V_1/V_2)$



(2) [Cycle: 1 → 2 → 4 → 1]

$$\Delta S_a = \Delta S_A + \Delta S_D + \Delta S_E = nR \times \ln\frac{V_2}{V_1} + C_V \times \ln\frac{T_3}{T_1} + C_V \times \ln\frac{T_1}{T_3} + nR \times \ln\frac{V_1}{V_2} = 0$$

✓ This result is again consistent with the fact that S is a state function.

1.3.1. The 2nd law of thermodynamics
- Some additional examples for entropy change calculation-

In following examples, we assume reversible processes. Thus, according to the first and the second laws

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

(Example-1) Determine the entropy change for a constant volume reversible process in a closed system (not isolated). Then, again determine it with further assuming the system is of an ideal gas.

As constant-volume ($dV = 0$): $dU = TdS$

From the definition of constant-volume heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$, then

$$\Delta S = S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{dU}{T} (const. V, N) = \int_{T_1}^{T_2} \frac{C_V}{T} dT (const. V, N)$$

If we further assume an ideal gas (which means C_V is a constant),

then: $\Delta S = C_V \ln \frac{T_2}{T_1}$

*Because the system is closed, not isolated, dS can be less than 0, and thus ΔS can be less than 0. (but during the process, $dS \geq \frac{\delta q}{T}$ is needed.)

1.3.1. The 2nd law of thermodynamics
- Some additional examples for entropy change calculation-

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

(Ex.2) Determine the entropy change for a constant pressure reversible process in a closed system (not isolated). Then, again determine it with further assuming the system is of an ideal gas.

As constant-pressure ($dP = 0$): $dH = \cdots$

From the definition of constant-pressure heat capacity: $dH = C_P dT$, then

If we assume an ideal gas (C_P=const.), then:

(Ex.3) Determine the entropy change for a constant temperature reversible process in a closed system (not isolated). Then, again determine it with further assuming the system is of an ideal gas.

As constant-temperature ($dT = 0$), if we assume an ideal gas: $dU = 0$

1.3.1. The 2nd law of thermodynamics
- Some additional examples for entropy change calculation-

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

(Ex.2) Determine the entropy change for a constant pressure reversible process in a closed system (not isolated). Then, again determine it with further assuming the system is of an ideal gas.

As constant-pressure ($dP = 0$)*:* $dH = dU + PdV + VdP = TdS$

From the definition of constant-pressure heat capacity: $C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N}$, then

$$\Delta S = S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{dH}{T}(const.\, P, N) = \int_{T_1}^{T_2} \frac{C_P}{T} dT(const.\, P, N)$$

If we assume an ideal gas, then: $\Delta S = C_P \ln \frac{T_2}{T_1}$

1.3.1. The 2nd law of thermodynamics
- Some additional examples for entropy change calculation-

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

(Ex.3) Determine the entropy change for a constant temperature reversible process in a closed system (not isolated). Then, again determine it with further assuming the system is of an ideal gas.

As constant-temperature ($dT = 0$)*, if we assume an ideal gas:* $dU = 0$

$$dS = \frac{P}{T}dV = nR\frac{dV}{V}$$

$$\Delta S = S(V_2, T) - S(V_1, T) = nR\int_{V_1}^{V_2}\frac{dV}{V} = nR\ln\frac{V_2}{V_1} = nR\ln\frac{P_1}{P_2}$$

Short review

-the first law and some typical conditions to specify a process-

- ✓ The first law of thermodynamics is an energy conservation law.

  $\mathrm{d}U = \delta q + \delta w, \quad \Delta U (= U_{final} - U_{initial}) = q + w$

  - ➢ Reversible process
    - ➢ For work, $P_{external} = P$. Thus, $\delta w = -PdV$
    - ➢ For heat, $q = q_{rev}$. Thus, $dS = \delta q/T$ thus $\delta q = TdS$
      - ➢ Combining these two, the first law is: $\mathrm{d}U = TdS - PdV$
  - ➢ Adiabatic process: $\delta q = 0$ thus $dU = \delta w$
  - ➢ Isothermal process :$dT = 0,$
    - ➢ Assuming an ideal gas ($U = U(T)$) : $dU = 0$ thus $\delta w = -\delta q$
  - ➢ Constant-volume process : $dV = 0$
    - ➢ Assuming only reversible P-V work:$\delta w = -\mathrm{Pd}V = 0$ thus $dU = \delta q$

- ✓ Internal energy (U) v.s. enthalpy (H) (in a reversible process):
  - ➢ The definition of enthalpy is: $H = U + PV$
  - ➢ Constant-volume process ($\delta w = -\mathrm{PdV} = 0$): $q = q_V = \Delta U$
  - ➢ Constant-pressure process ($dP = 0$): $q = q_P = \Delta U + P\Delta V = \Delta H$

    *$\Delta H = \Delta(U + PV) = \Delta U + P\Delta V + V\Delta P = \Delta U + P\Delta V.$

Short review
-the first law and some typical conditions to specify a process-

- ✓ Internal energy (U) v.s. enthalpy (H) (in a reversible process):
  - ➢ Constant-volume process ($\delta w = \mathrm{PdV} = 0$): $q = q_V = \Delta U$
  - ➢ Constant-pressure process ($dP = 0$): $q = q_P = \Delta U + P\Delta V = \Delta H$

    *$\Delta H = \Delta(U + PV) = \Delta U + P\Delta V + V\Delta P = \Delta U + P\Delta V$.

- ✓ "Heat capacity" (*C* in $\mathrm{q} = C\Delta T$; heat capacity is a path function!) along specific paths, namely constant-volume and constant-pressure, are:

$$\boxed{q_V = \Delta U \longrightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}} \Longleftrightarrow \boxed{q_P = \Delta H \longrightarrow C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N}}$$

- ✓ Please be sure that $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N}$ and $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N}$ do not involve any assumptions. These equations are <u>definitions</u> of C_V and C_P.
  - ✓ If we assume the system is ideal gas, $C_V = \frac{dU}{dT}$ and $C_p = \frac{dH}{dT}$ are achieved. However, these equations are correct only for ideal gas (although reasonably accurate for most gasses under wide conditions).

(Appendix)
- Mathematics (chapter H): total derivative -

We consider a case of F for “F is a sole function of x, namely $F = F(x)$”

The derivative of F can be written as:

$$\frac{dF}{dx} = \lim_{\Delta x \to 0} \frac{F(x + \Delta x) - F(x)}{\Delta x}$$

We consider a case of F for “F is a function of x and y, namely $F = F(x, y)$”

The partial derivative of F with respect to x, with y held constant, can be *written as:*

$$\left(\frac{\partial F}{\partial x}\right)_y = \lim_{\Delta x \to 0} \frac{F(x + \Delta x, y) - F(x, y)}{\Delta x}$$

As the same way, “F is a function of x, y and z, namely $F = F(x, y, z)$”, for example

$$\left(\frac{\partial F}{\partial x}\right)_{y,z} = \lim_{\Delta x \to 0} \frac{F(x + \Delta x, y, z) - F(x, y, z)}{\Delta x}$$

(Appendix)
- Mathematics (chapter H): total derivative -

We consider a case of F for “F is a function of x and y, namely $F = F(x, y)$”

The total derivative of F can be written as:

$$\Delta F = F(x + \Delta x, y + \Delta y) - F(x, y)$$
$$= [F(x + \Delta x, y + \Delta y) - F(x, y + \Delta y)] + [F(x, y + \Delta y) - F(x, y)]$$
$$= \left[\frac{F(x + \Delta x, y + \Delta y) - F(x, y + \Delta y)}{\Delta x}\right] \Delta x + \left[\frac{F(x, y + \Delta y) - F(x, y)}{\Delta y}\right] \Delta y$$

Then let $\Delta x \to 0$ *and* $\Delta y \to 0$ *as:*

$$dF$$
$$= \lim_{\Delta x \to 0} \left[\frac{F(x + \Delta x, y + \Delta y) - F(x, y + \Delta y)}{\Delta x}\right] \Delta x + \lim_{\Delta x \to 0} \left[\frac{F(x, y + \Delta y) - F(x, y)}{\Delta y}\right] \Delta y$$
$$= \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

(Appendix)
- Mathematics (chapter H): total derivative -

As the same way, for “F is a function of x, y and z, namely $F = F(x, y, z)$”, the total derivative F can be written as:

$$dF = \left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{z,x} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y} dz$$

Here, if $\left(\frac{\partial F}{\partial z}\right)_{x,y} dz$ is nearly 0, namely $\left(\frac{\partial F}{\partial z}\right)_{x,y}$ or Δz is nearly 0 (or much smaller than those for x and y, it can be approximated with an minimal error as:

$$dF \sim \left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{z,x} dy$$

1.3.2. The 3rd law of thermodynamics
- temperature dependence of entropy -

If we treat U and S as functions of V and T thus U(T, V) and S(T, V), their total derivatives are:

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

As the first and second laws for a reversible process:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

$$\boxed{C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V}$$

The definition of C_V

By substituting this equation to the first one:

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV = \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

In comparison with the total derivative of S given above:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

1.3.2. The 3rd law of thermodynamics
- temperature dependence of entropy (cont'd)-

Based on the first and second laws for a reversible process, and assumptions that U(T, V) and S(T, V):

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

By making an integral with respect to T (with keeping V constant):

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

Hence, we can calculate S of an arbitrary temperature, S(T), if we know S(0 K):

$$S(T) = S(0\ K) + \int_0^T \frac{C_V(T')dT'}{T'} \qquad \text{(constant V, (constant N))}$$

**Note that we do not assume ideal gas to obtain this equation.*

In an analogy, if we go through similar steps under constant pressure case (we start with the total derivative of H(S,P)):

$$S(T) = S(0\ K) + \int_0^T \frac{C_P(T')dT'}{T'} \qquad \text{(constant P, (constant N))}$$

1.3.2. The 3rd law of thermodynamics
- the definition of a numerical scale for entropy-

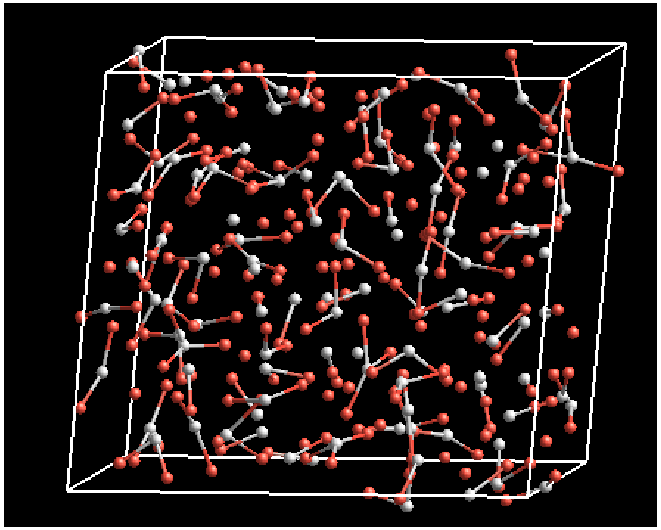
- ✓ Nernst and Planck made a postulate corresponding to the third law:

> Every substance has a finite positive entropy, but at zero kelvin the entropy may become zero, and does so in the case of a perfectly crystalline substance.

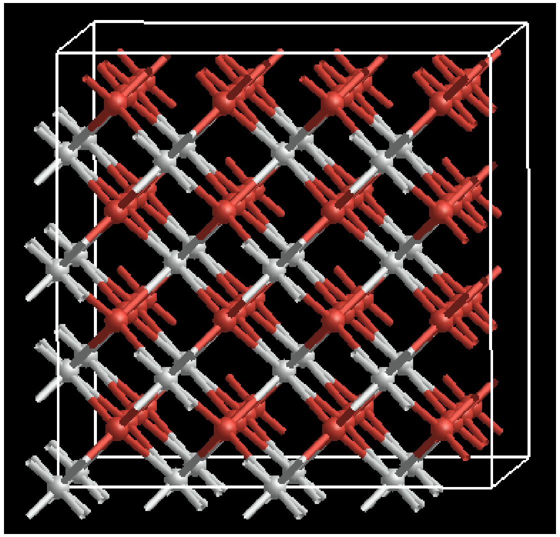
*We assume the state at 0 K is a perfect crystal. This is reasonable because

- ➢ A material becomes a solid at low temperatures.
- ➢ Entropy is related to disorder of the system.(we will learn latter)
- ➢ The lowest entropy must be achieved with the lowest disorder, which is the perfect crystal.

Liquid of UO_2



Perfect crystal of UO_2

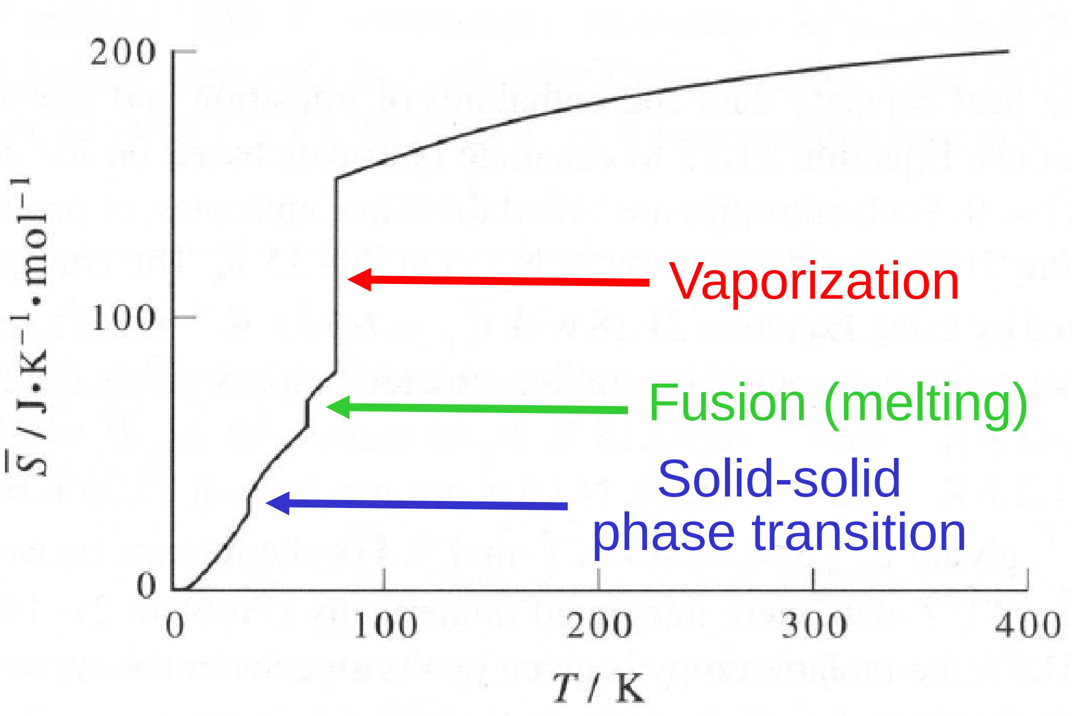


1.3.2. The 3rd law of thermodynamics
- an example of temperature dependence of entropy-

TABLE 21.1

The standard molar entropy of nitrogen at 298.15 K.

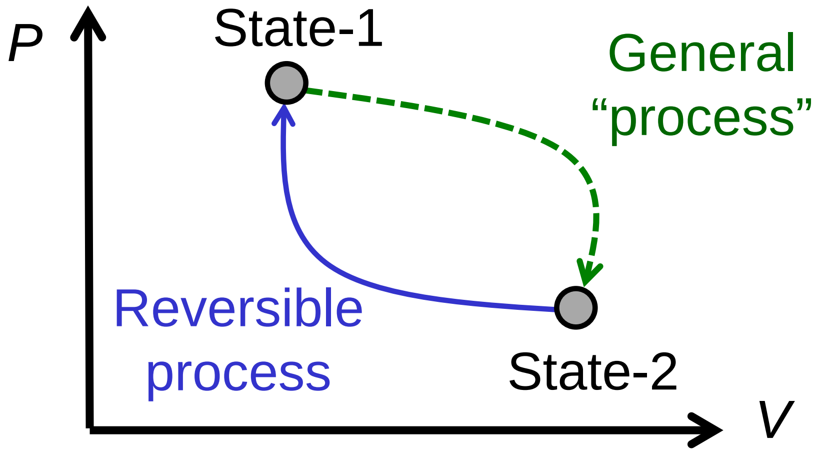
Process	$\overline{S}^{\circ}$/J·K^{-1}·mol^{-1}
0 to 10.00 K	2.05
10.00 to 35.61 K	25.79
Transition	6.43
35.61 to 63.15 K	23.41
Fusion	11.2
63.15 to 77.36 K	11.46
Vaporization	72.0
77.36 K to 298.15 K	39.25
Correction for nonideality	0.02
Total	191.6



Temperature dependence of the molar entropy of nitrogen

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

1.3.X. How to judge whether reversible or irreversible
- entropy change in a process -



- ✓ For this cycle composed of 2 processes, Clausius theorem gives:

$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q}{T} + \int_2^1 \frac{\delta q_{rev}}{T} \leq 0$$ then $$\int_1^2 \frac{\delta q}{T} \leq \int_1^2 \frac{\delta q_{rev}}{T} = \int_1^2 dS = S_2 - S_1 = \Delta S$$

where the equal sign is achieved when the general process is reversible and the unequal sign is achieved when the general process is irreversible.

$$dS \geq \frac{\delta q}{T} \qquad \Delta S = \int_1^2 dS = S_2 - S_1 \geq \int_1^2 \frac{\delta q}{T}$$

1.3.X. How to judge whether reversible or irreversible
- entropy change/production/exchange-

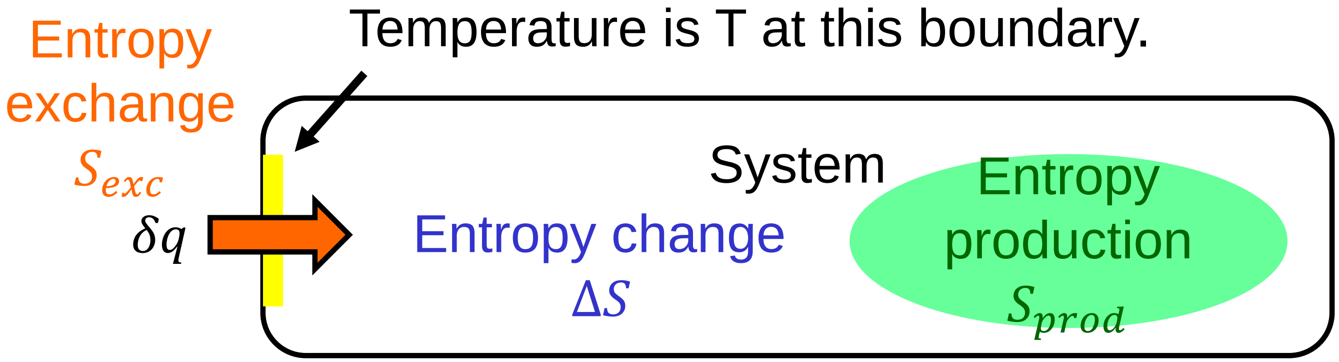
$$\underbrace{\Delta S = \int_1^2 dS = S_2 - S_1}_{\substack{\text{Entropy change} \\ \text{(state function)}}} \geq \underbrace{\int_1^2 \frac{\delta q}{T}}_{\substack{\text{Entropy exchange} \\ \text{(path function)}}}$$

*the equal sign is achieved when the process is reversible and the unequal sign is achieved when the process is irreversible.

✓ This means that entropy change is larger than entropy transfer if the process is irreversible. Then, we define “entropy production” (entropy generation) to indicate the degree of “irreversibility” of the process.

$$S_{prod} = (S_2 - S_1) - \int_1^2 \frac{\delta q}{T} = \Delta S - S_{exc} \geq 0$$

$$dS = \delta S_{prod} + \delta S_{exc}$$



Temperature is T at this boundary.

Entropy exchange S_{exc}

δq

System

Entropy change ΔS

Entropy production S_{prod}

1.3.X. How to judge whether reversible or irreversible
- a theoretical way to judge-

✓ We divide dS into two types:

- ➢ δS_{prod} : due to the irreversible process, which is produced inside the system (≥ 0, where the equal sign is achieved if reversible process).
- ➢ δS_{exc} : due to the exchange of energy as heat with the surroundings, and defined as δq/T which can take any value.

$$dS = \delta S_{prod} + \delta S_{exc} = \delta S_{prod} + \frac{\delta q}{T} \geq \frac{\delta q}{T} \qquad dS = \frac{\delta q_{rev}}{T}$$

(1) For a reversible process, which does not produce the entropy inside the system ($\delta S_{prod} = 0$), $dS = \frac{\delta q}{T}$ as $\delta q = \delta q_{rev}$.

(2) For an irreversible, which produces the entropy inside the system ($\delta S_{prod} > 0$):$dS > \frac{\delta q}{T}$ where $\delta q = \delta q_{irr}$

So, if we can calculate $\frac{\delta q}{T}$ or $\int \frac{\delta q}{T}$ of a concerned process, and then compare it with dS or ΔS, which can be determined using imaginary reversible process, we can judge whether the process is reversible or irreversible.

1.3.X. How to judge whether reversible or irreversible
- entropy change/production/exchange-

Let’s check some examples using the following equation that we derived in the homework.

[HW01-10:#20-14]

(1) Please show that

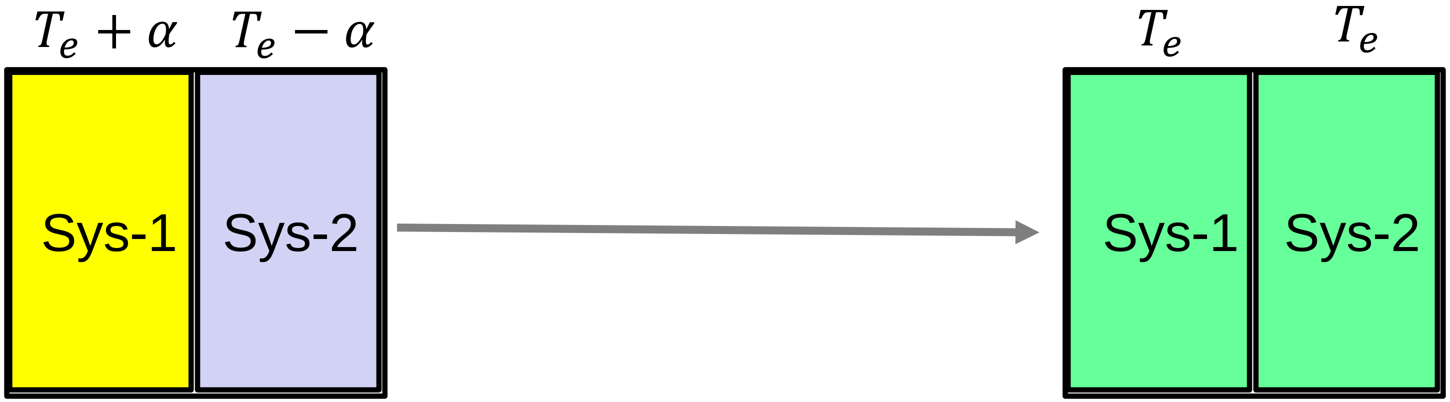
$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

when 1 mole of an ideal gas is taken from state-1 (T_1, V_1) to state-2 (T_2, V_2), assuming that C_V (constant-volume heat capacity) is independent of temperature.

1.3.X. How to judge whether reversible or irreversible -(Example-1) energy transfer as heat between 2 systems-

We consider a connected system (sys-1 and sys-2):

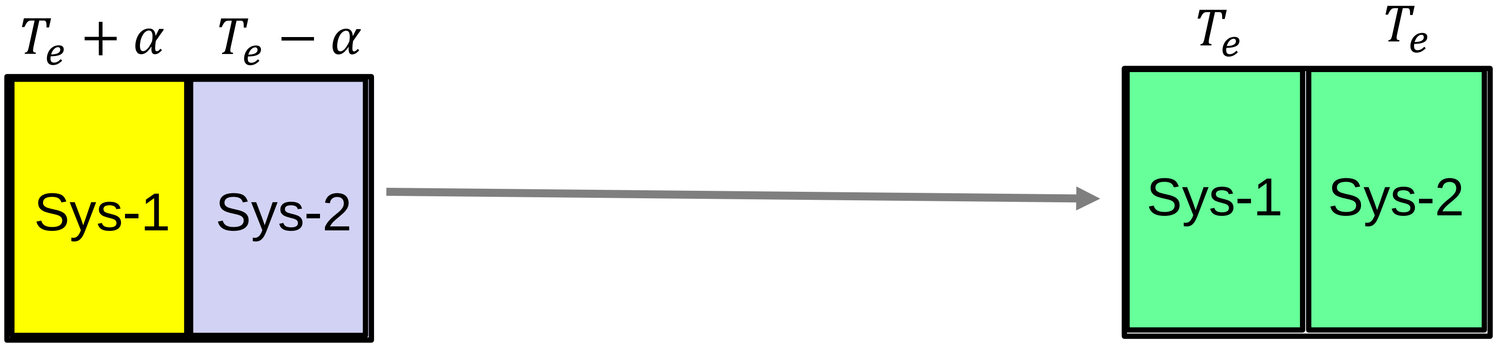
- ✓ These systems are composed of the same sort of ideal gas having the same amount (n mol) and heat capacity.
- ✓ These two system can exchange neither mass nor energy with the surroundings.
- ✓ These two systems can exchange energy as heat with each other. Sys-1 is of higher temperature ($T_e + \alpha$) than sys-2 ($T_e - \alpha$).
- ✓ The volume are constant during the process, thus this is constant-volume cooling for Sys-1 and heating for Sys-2.



1.3.X. How to judge whether reversible or irreversible -(Example-1) energy transfer as heat between 2 systems-

$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

by a process from state-1 (T_1, V_1) to state-2 (T_2, V_2) for ideal gas



Using the entropy change expression for the ideal gas,

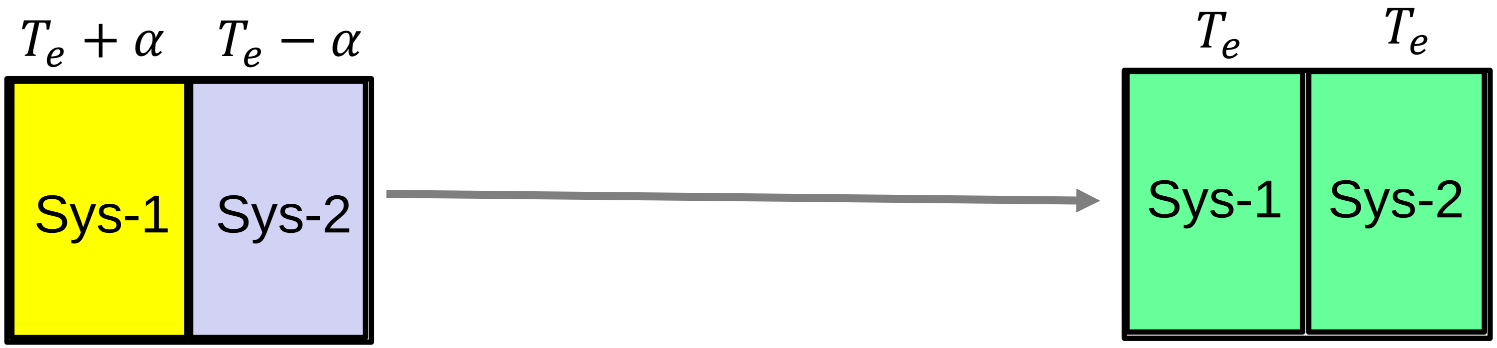
$$\Delta S_1 = C_V \ln\frac{T_{fin}}{T_{ini}} = C_V \ln\frac{T_e}{T_e + \alpha} \qquad \Delta S_2 = C_V \ln\frac{T_{fin}}{T_{ini}} = C_V \ln\frac{T_e}{T_e - \alpha}$$

If we consider these 2 systems as a 1 combined system, this system is regarded as an isolated system as no energy and no mass were transferred in this internal process. Then,

$$\Delta S_{comb-sys} = \Delta S_1 + \Delta S_2 = C_V \ln\frac{T_e}{T_e + \alpha} + C_V \ln\frac{T_e}{T_e - \alpha} = C_V \ln\frac{{T_e}^2}{{T_e}^2 - \alpha^2} > 0$$

In this process, $S_{exc} = 0$ as fro the new system. Thus, $\Delta S_{comb-sys} = S_{prod} > 0$

1.3.X. How to judge whether reversible or irreversible -(Example-1) energy transfer as heat between 2 systems-



$$\Delta S_{comb-sys} = S_{prod} = C_V \ln \frac{T_e{}^2}{T_e{}^2 - \alpha^2} > 0$$

- ✓ This equation means that "energy transfer as heat between two systems (or between the system and the surroundings) of different temperatures is irreversible process".

- ✓ If $\alpha = 0$, $\Delta S_{comb-sys} = S_{prod} = 0$ is achieved. So, "energy transfer as heat between two systems (or b/w the system and the surroundings) of the same temperature is reversible process." This "same temperature" can be replaced with systems of infinitesimal temperature gap, like $\alpha \rightarrow 0$.

1.3.X. How to judge whether reversible or irreversible

- a practical way to judge -

- ✓ In energy transfer as heat, which is driven by temperature difference:
  - ✓ If the temperature difference is infinitesimal, $\delta S_{prod} = 0$, thus the process is reversible.
  - ✓ If the temperature difference is not negligible, $\delta S_{prod} > 0$, thus the process is irreversible.

    e.g.) heat transfer from a higher temperature object to a lower temperature object. ($T_{sys} \neq T_{ext}$)

- ✓ Likewise, in energy transfer as work, which is driven by pressure (force, stress, etc) difference:
  - ✓ If the pressure difference is infinitesimal, $\delta S_{prod} = 0$, thus the process is reversible.
  - ✓ If the pressure difference is not negligible, $\delta S_{prod} > 0$, thus the process is irreversible.

    e.g.) expansion to a vacuum. ($P_{sys} \neq P_{ext}$)

1.3.X. How to judge whether reversible or irreversible
- what is "reversible heating"?-

- ✓ If heat transfer occurs between two objects having different temperatures, the process is not reversible.

- ✓ To avoid this situation in concept, we consider a infinite number of thermostats having slightly different temperatures, like $T_1 = T_{ini} + \Delta T$, $T_2 = T_{ini} + 2\Delta T$, ..., where

$$\Delta T = \lim_{N \to \infty} \frac{T_{fin} - T_{ini}}{N}$$

- ✓ Then, the system is sequentially connected to a thermostat having infinitesimally higher temperature one be one.
  - ➢ Isothermal processes are more simple because heat transfer occurs with the surroundings having the same temperature with the system.

- ✓ "Reversible expansion/compression" is also such very unrealistic process to avoid the pressure gap during the process.
  - ➢ Constant-pressure process is more simple as well.