Spontaneity of Chemical Reactions

We are going to define a new state function that will define the direction of spontaneous processes. This state function is the entropy.

Entropy is related to heat and heat flow and yet heat is not a state function. Recall that q is a path function. It turns out that the state function needed to describe spontaneous change is the heat divided by the temperature.
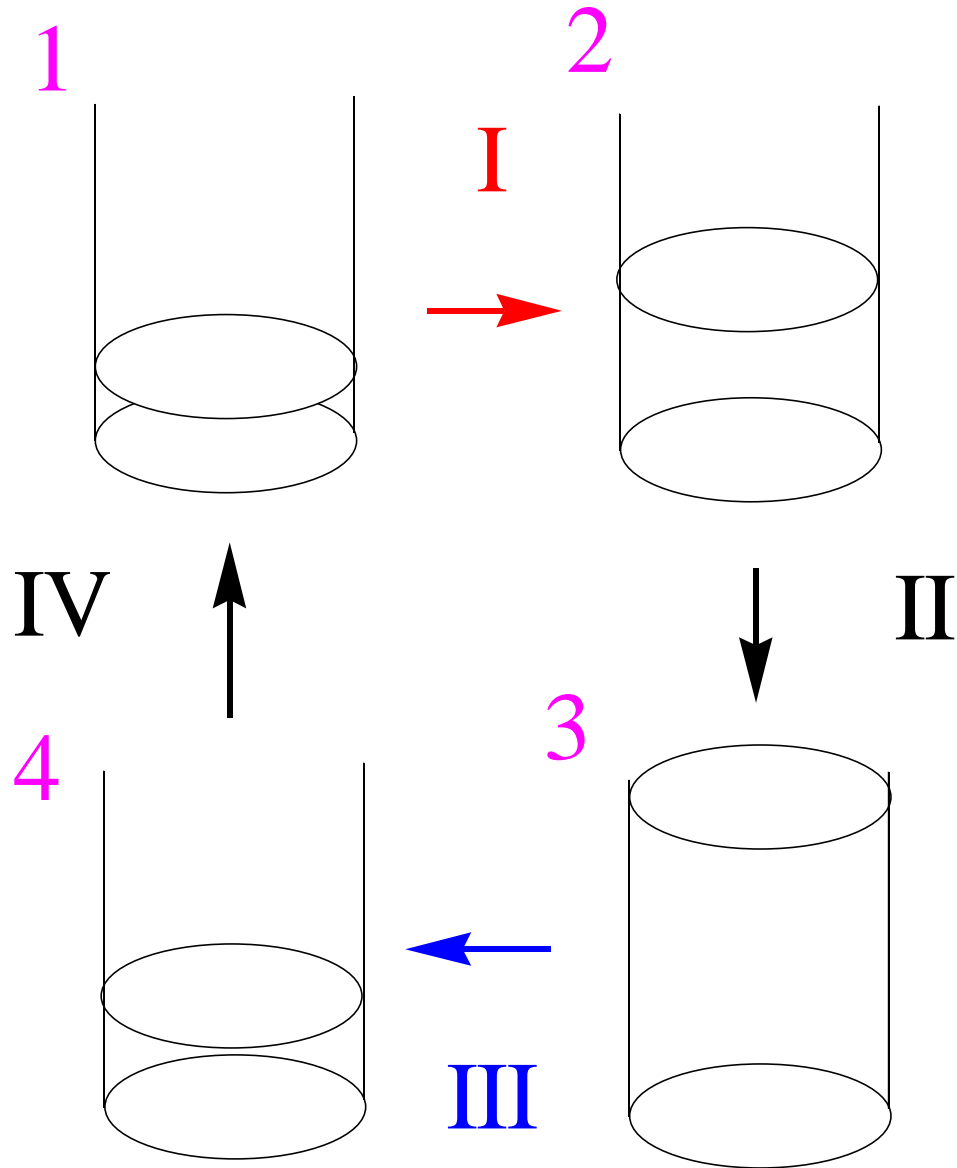Here we simply state this result.

$$\Delta S = \frac{q_{rev}}{T}$$

We will prove that entropy is a state function in this lecture.

Engines

Historically, people were interested in understanding the efficiency with which heat is converted into work. This was a very important question at the dawn of the industrial revolution since it was easy to conceive of an engine powered by steam, but it turned out to be quite difficult to build one that was efficient enough to get anything done! In an engine, there is a cycle in which fuel is burned to heat gas inside the piston. The expansion of the piston leads to cooling and work. Compression readies the piston for the next cycle. A state function should have zero net change for the cycle. It is only the state that matters to such a function, not the path required to get there. Heat is a path function. As we all know in an internal combustion engine (or a steam engine), there is a net release of heat. Therefore, we all understand that $\delta q \neq 0$ for the cycle.
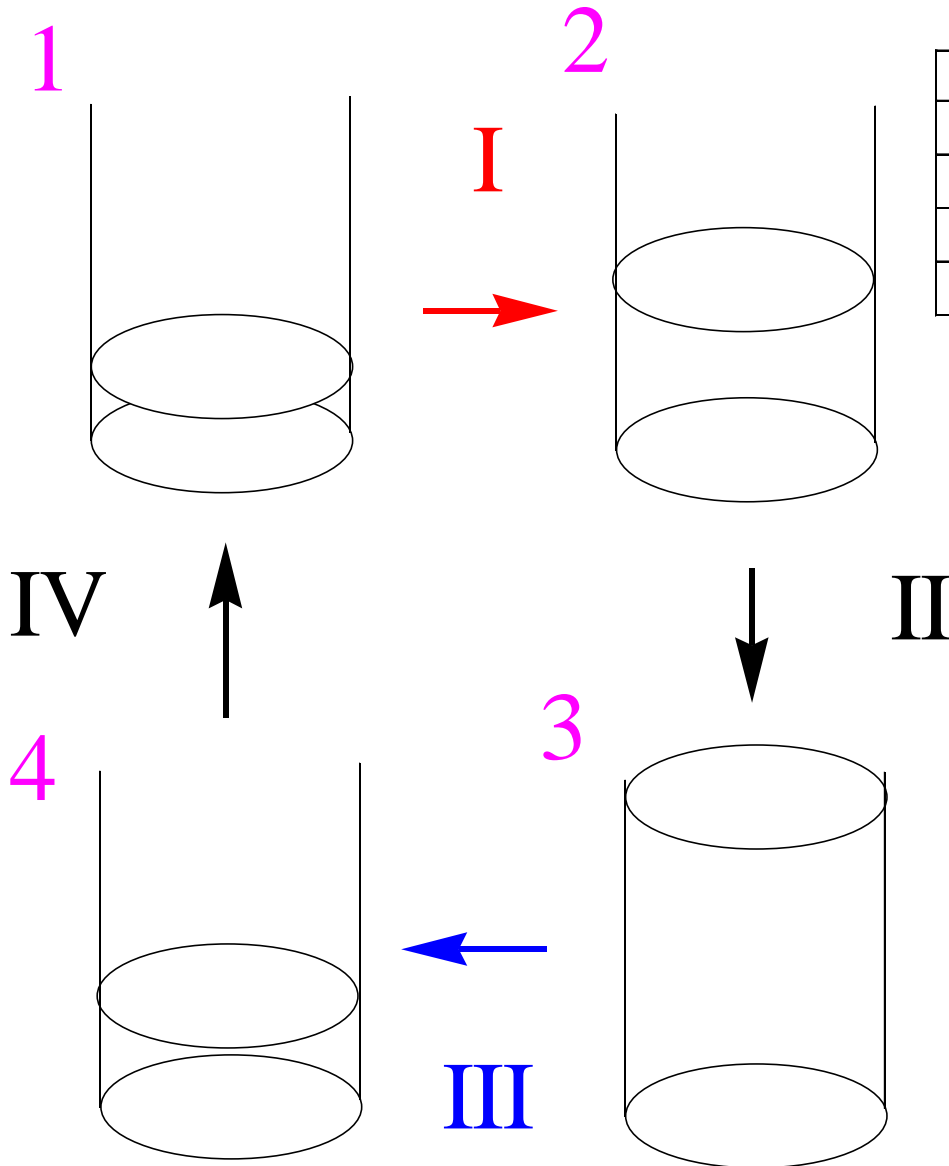
A cyclic heat engine
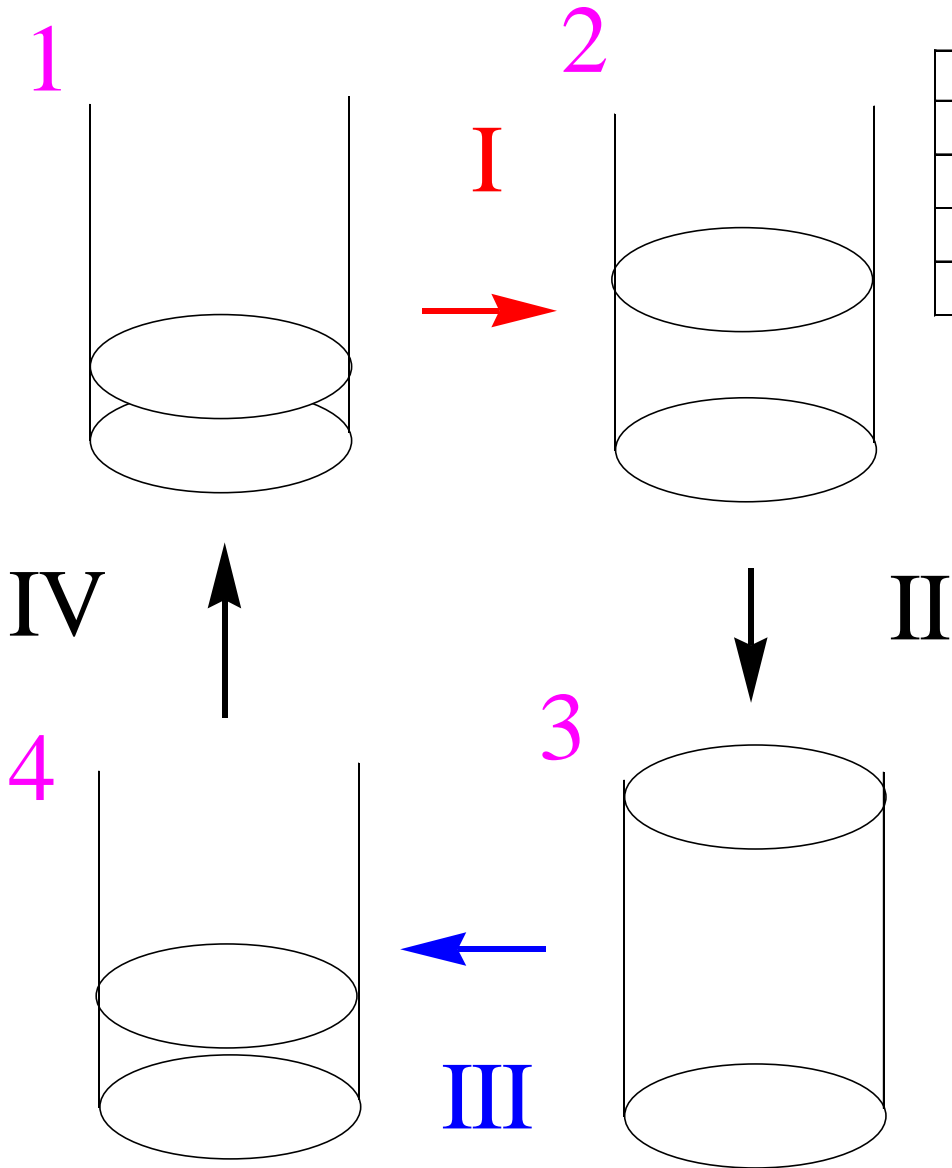
1

2

I

IV

II

4

3

III

A cyclic heat engine

Phase	Transition	Path	Condition
I.	1→2	Isothermal	w = -q
II.	2→3	Adiabatic	$\Delta U = w$
III.	3→4	Isothermal	w = -q
IV.	4→1	Adiabatic	$\Delta U = w$

A cyclic heat engine

1

2

I

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IV.	4→1	Adiabatic	$\Delta U = w$

IV

II

The work is

$$w = w_I + w_{II} + w_{III} + w_{IV}$$
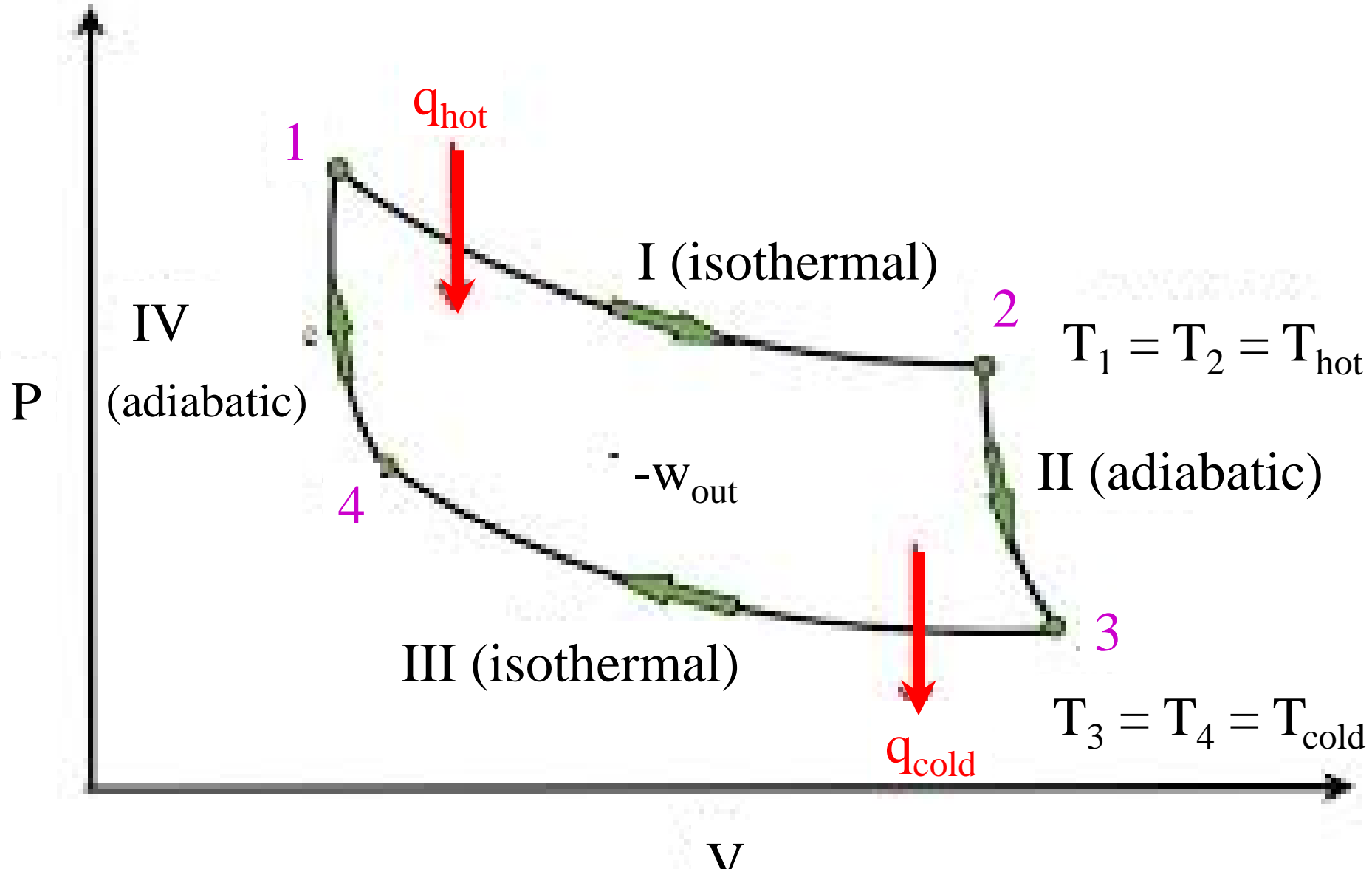
$$q = q_I + q_{III}$$

$$= - w_I - w_{III}$$

3

4

For the adiabatic steps

$$q_{II} = q_{IV} = 0$$

For the isothermal steps

$$\Delta U = 0$$

III

Work and Heat for the Cycle

 Neither the work nor the heat is a state function. Neither one is zero for the cycle as should be the case for a state function. The work is:

$w = w_I + w_{II} + w_{III} + w_{IV}$

$= -nRT_{hot}\ln(V_2/V_1) + C_v(T_{cold} - T_{hot}) - nRT_{cold}\ln(V_4/V_3) + C_v(T_{hot} - T_{cold})$

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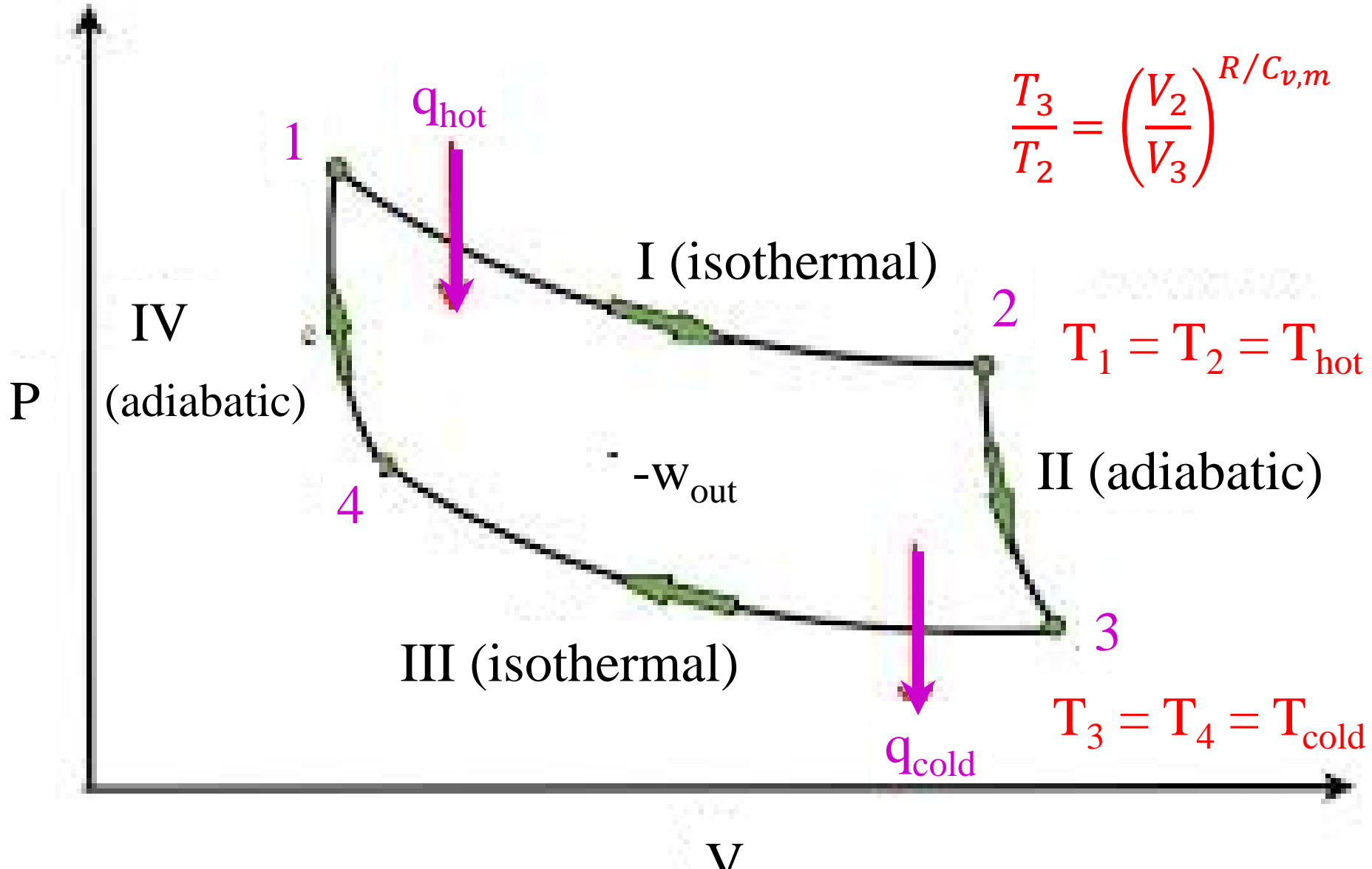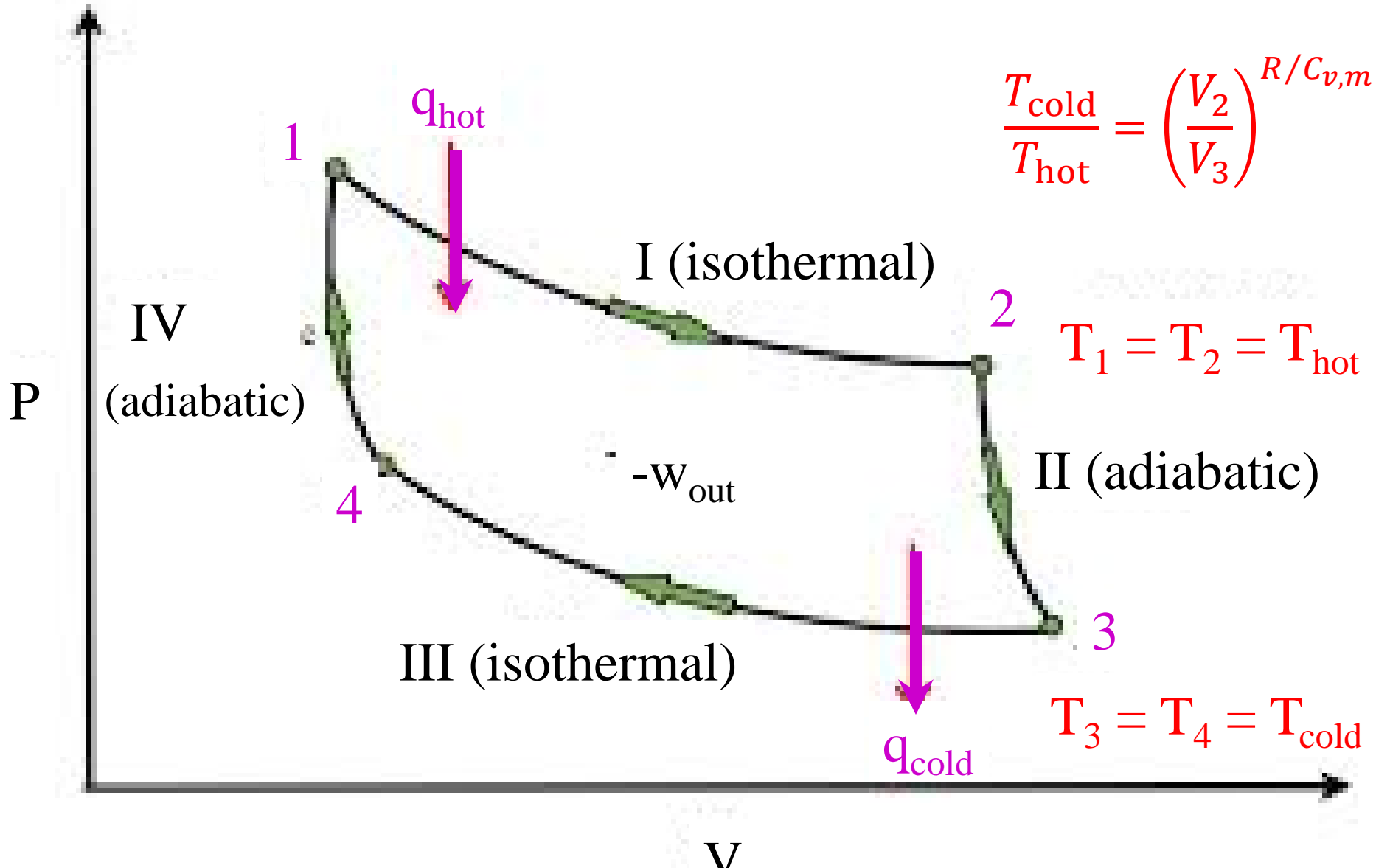
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$w = -nRT_{hot}\ln(V_2/V_1) - nRT_{cold}\ln(V_4/V_3)$ [since $w_{II} = -w_{IV}$]

$$\frac{T_1}{T_4} = \left(\frac{V_4}{V_1}\right)^{R/C_{v,m}}$$

$$\frac{T_3}{T_2} = \left(\frac{V_2}{V_3}\right)^{R/C_{v,m}}$$

P

V

1

2

3

4

q_{hot}

q_{cold}

$-w_{out}$

I (isothermal)

II (adiabatic)

III (isothermal)

IV (adiabatic)

$T_1 = T_2 = T_{hot}$

$T_3 = T_4 = T_{cold}$

$$\frac{T_{\text{hot}}}{T_{cold}} = \left(\frac{V_4}{V_1}\right)^{R/C_{v,m}}$$

$$\frac{T_{\text{cold}}}{T_{\text{hot}}} = \left(\frac{V_2}{V_3}\right)^{R/C_{v,m}}$$

q_{hot}

P

1

I (isothermal)

IV

(adiabatic)

2

$T_1 = T_2 = T_{\text{hot}}$

-w$_{\text{out}}$

II (adiabatic)

4

III (isothermal)

3

q_{cold}
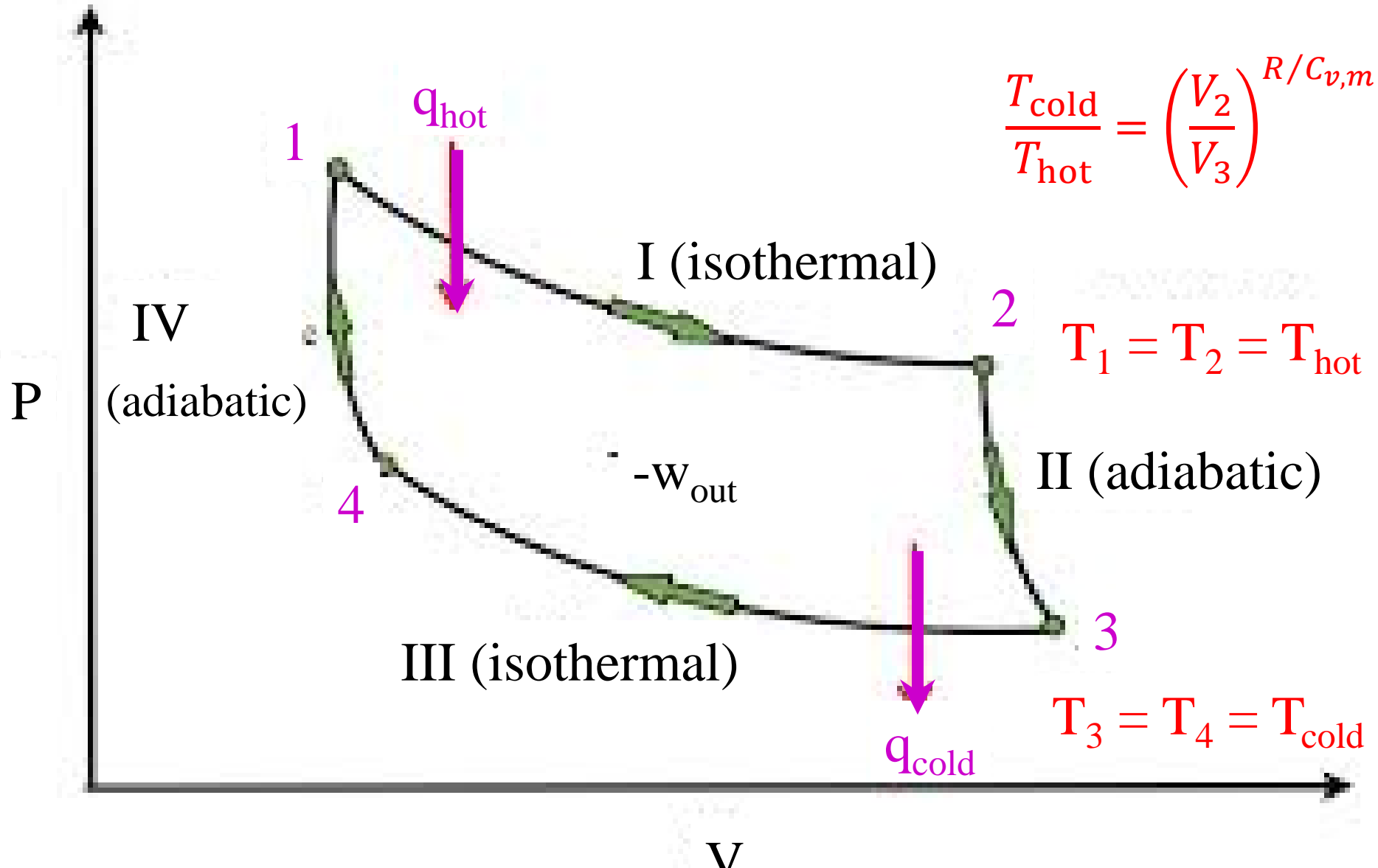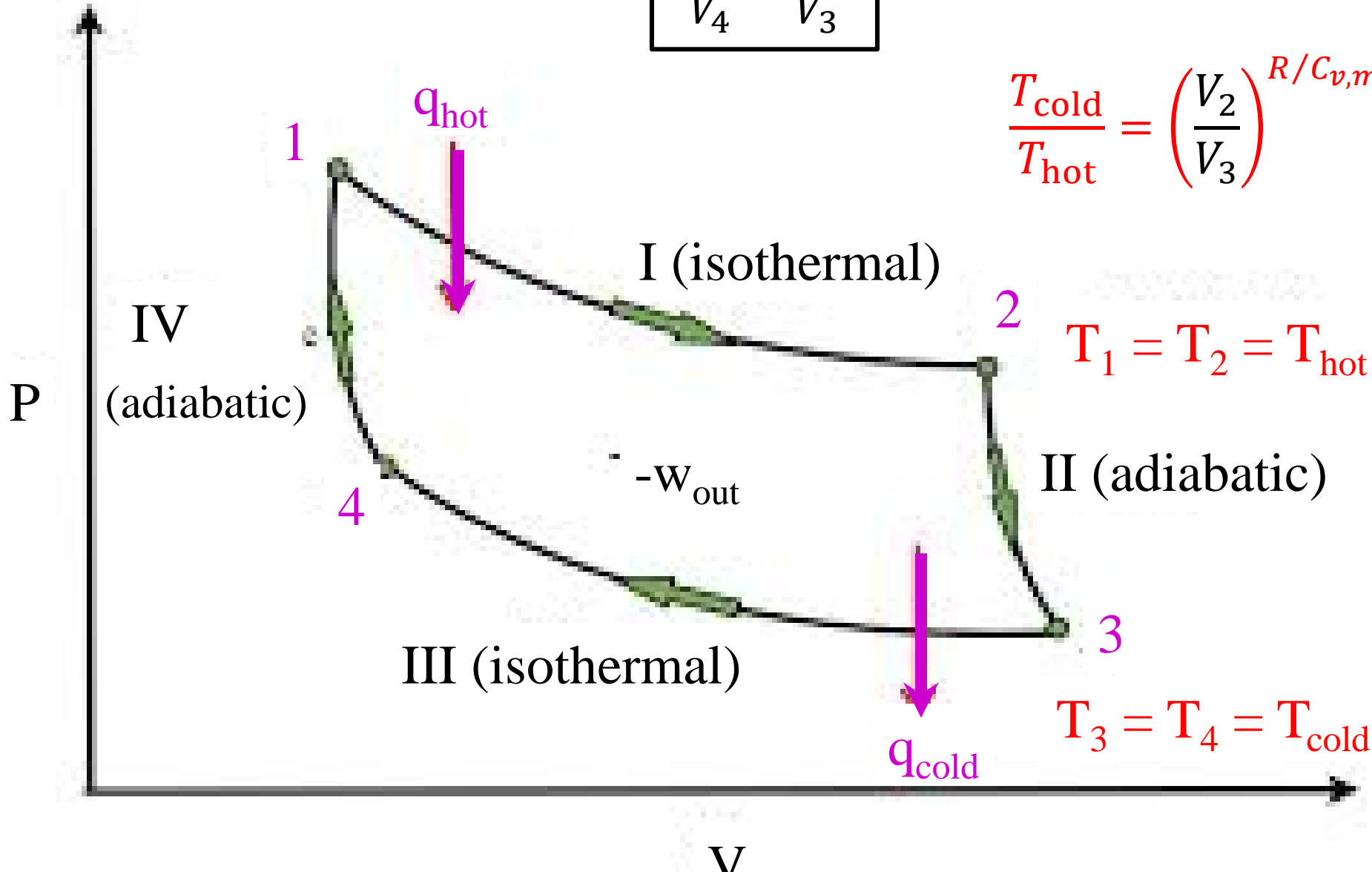
$T_3 = T_4 = T_{\text{cold}}$

V
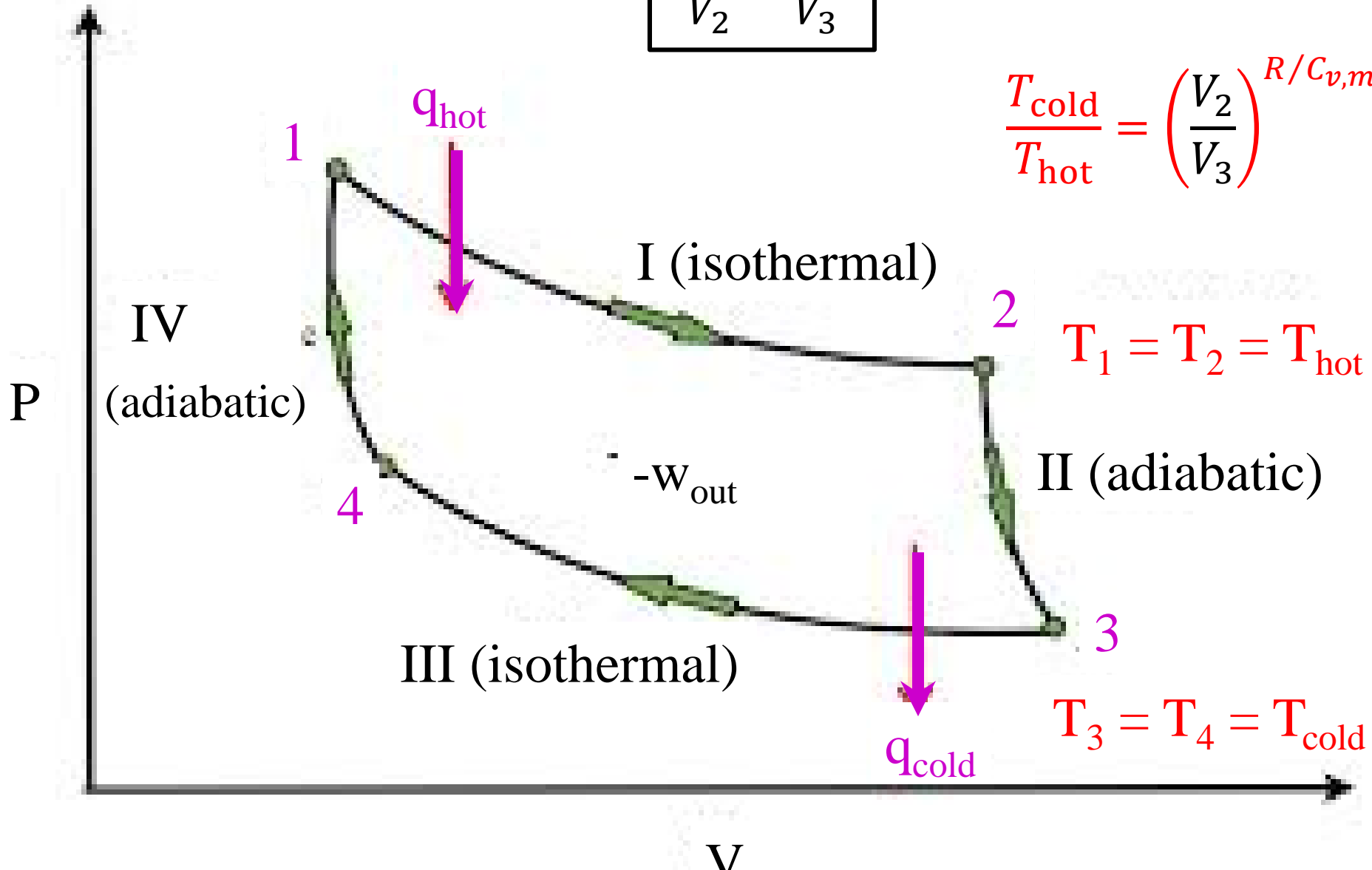
$$\frac{T_{\text{cold}}}{T_{hot}} = \left(\frac{V_1}{V_4}\right)^{R/C_{v,m}}$$

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q_{hot}

1

I (isothermal)

2

$T_1 = T_2 = T_{\text{hot}}$

IV (adiabatic)

P

$-w_{\text{out}}$

II (adiabatic)

4

III (isothermal)

3

q_{cold}

$T_3 = T_4 = T_{\text{cold}}$

V

$$\frac{T_{cold}}{T_{hot}} = \left(\frac{V_1}{V_4}\right)^{R/C_{v,m}}$$

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q_{hot}

I (isothermal)

IV (adiabatic)

2

$T_1 = T_2 = T_{hot}$

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3

q_{cold}

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P

V

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1

IV

(adiabatic)

2

$T_1 = T_2 = T_{\text{hot}}$

II (adiabatic)

$-w_{\text{out}}$

4

3

III (isothermal)

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$T_3 = T_4 = T_{\text{cold}}$

P

V

Work and Heat for the Cycle

Neither the work nor the heat is a state function. Neither one is zero for the cycle as should be the case for a state function. The work is:

$w = w_I + w_{II} + w_{III} + w_{IV}$

$=-nRT_{hot}\ln(V_2/V_1)+C_v(T_{cold}-T_{hot})-nRT_{cold}\ln(V_4/V_3)+C_v(T_{hot}-T_{cold})$

$w = -nRT_{hot}\ln(V_2/V_1) - nRT_{cold}\ln(V_4/V_3)$

$w = -nRT_{hot}\ln(V_2/V_1) - nRT_{cold}\ln(V_1/V_2)$ [since $V_4/V_3 = V_1/V_2$]

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$w = -nRT_{hot}\ln(V_2/V_1) + nRT_{cold}\ln(V_2/V_1)$ [property of logarithms]

The heat is:

$q = q_I + q_{III}$ [since $q_{II} = q_{IV} = 0$ for adiabatic processes]

$= -w_I - w_{III}$ [since $dU = 0$ for isothermal steps]

$q = nRT_{hot}\ln(V_2/V_1) + nRT_{cold}\ln(V_4/V_3)$

$q = nRT_{hot}\ln(V_2/V_1) + nRT_{cold}\ln(V_1/V_2)$ [since $V_4/V_3 = V_1/V_2$]

$q = nRT_{hot}\ln(V_2/V_1) - nRT_{cold}\ln(V_2/V_1)$ [property of logarithms]

A new state function: Entropy

The heat is not a state function. The sum $q_I + q_{III}$ is not zero. From this point on we will make the following definitions:

$$q_I = q_{hot} \qquad q_{III} = q_{cold}$$

$$q = q_{hot} + q_{cold} = nRT_{hot}\ln\left(\frac{V_2}{V_1}\right) - nRT_{cold}\ln\left(\frac{V_2}{V_1}\right) \neq 0$$

$$\frac{q_{rev}}{T} = \frac{q_{hot}}{T_{hot}} + \frac{q_{cold}}{T_{cold}} = nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) = 0$$

However, the heat divided by temperature is a state function. This reasoning leads to the idea of a state function called the entropy. We can write:

$$\Delta S = \frac{q_{rev}}{T}$$