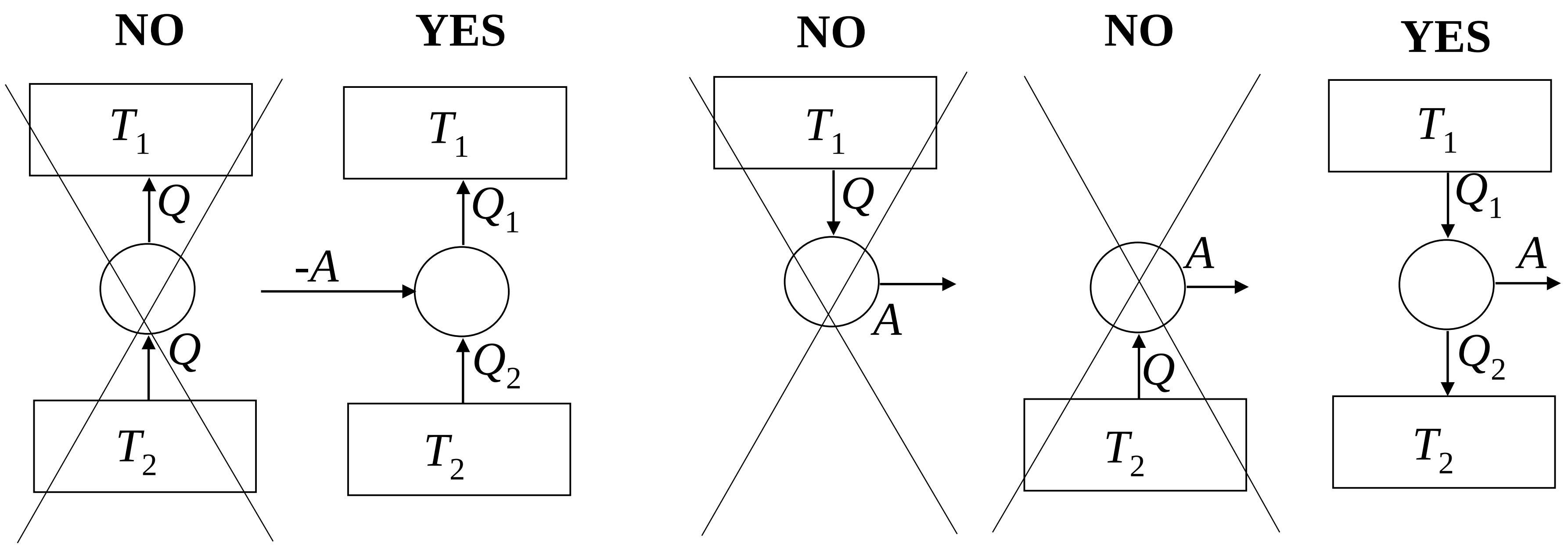
First law of thermodynamics $dQ = dU + dA$

Second law of thermodynamics



Clausius definition

Thomson definition

efficiency $\eta = \dfrac{\text{energy we get}}{\text{energy we pay for}}$

$\eta < 100\ \%$

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Entropy

$$dS \geq \frac{dQ}{T}$$

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T}$$

reversible processes

$$dQ = dU + dA$$

$$dS = \frac{dQ}{T} = n\frac{C_{mV}}{T}dT + \frac{p}{T}dV = n\frac{C_{mV}}{T}dT + n\frac{R_m}{V}dV$$

$$S_2 - S_1 = nC_{mV}\int_1^2 \frac{dT}{T} + nR_m\int_1^2 \frac{dV}{V} = nC_{mV}\ln\frac{T_2}{T_1} + nR_m\ln\frac{V_2}{V_1}$$

$$\int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ}{T} = \oint dS = 0$$

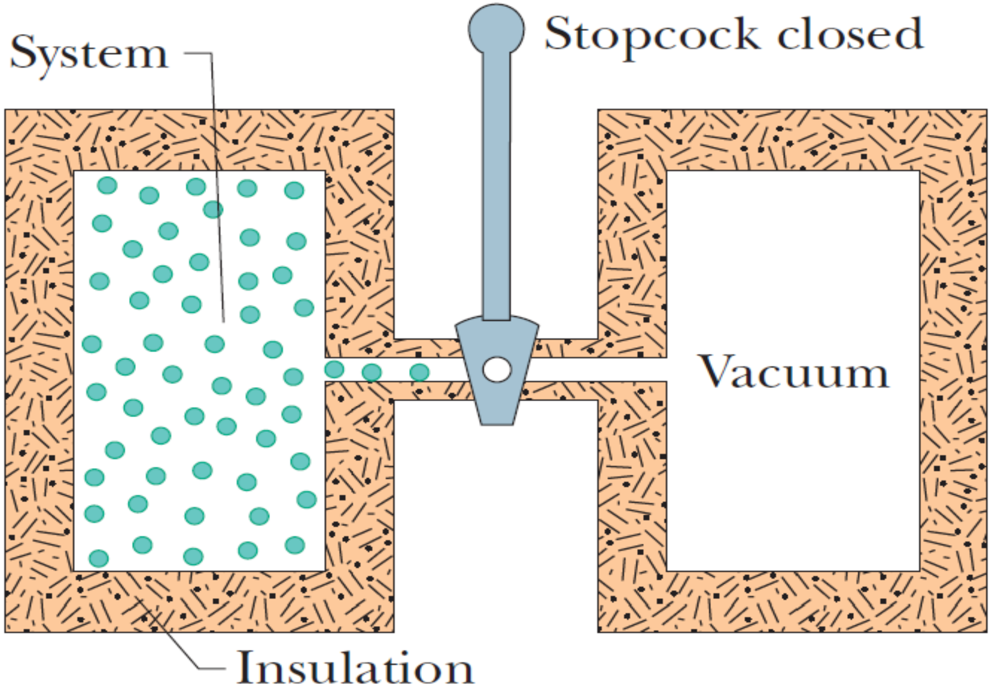
Adiabatic gas expansion free expansion

$$Q = A = 0 \;\Rightarrow\; \Delta U = 0$$

irreversible process

$$pV^{\kappa} = \text{const.}$$

$$\Delta S = nR_m \ln \frac{V_2}{V_1}$$



$$\Delta S = S_2 - S_1 \geq \int_1^2 \frac{dQ}{T}$$

If an irreversible process occurs in a closed system, the entropy of the system always increases; it never decreases. In the steady-state, the entropy of the system reaches the maximum.

$$\oint \frac{dQ}{T} \geq 0$$

= 0 for reversible processes

second law of thermodynamics – mathematical expression

$$\Delta S = S_2 - S_1 = k \ln W$$

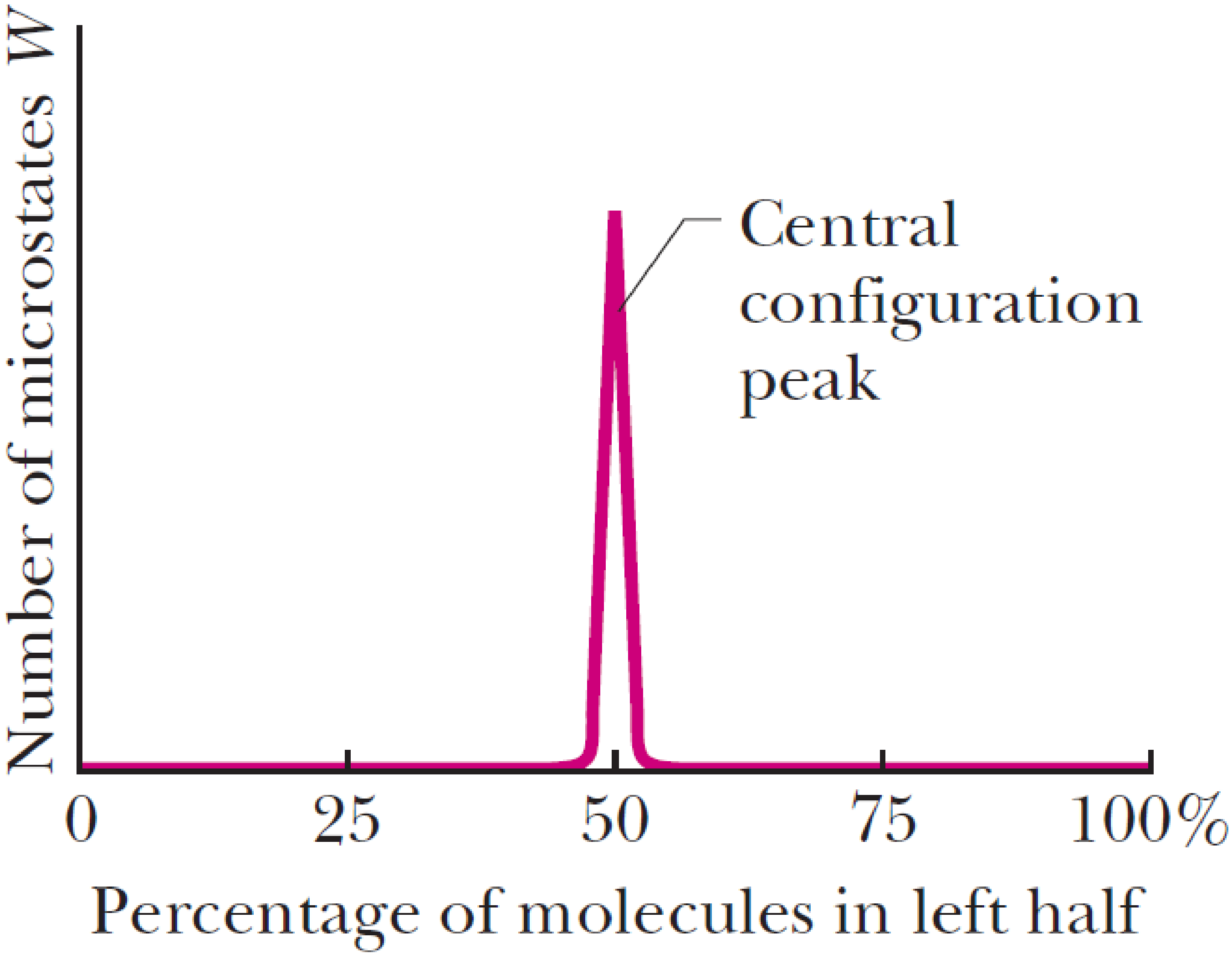
Boltzmann law

multiplicity of the microstates *W*

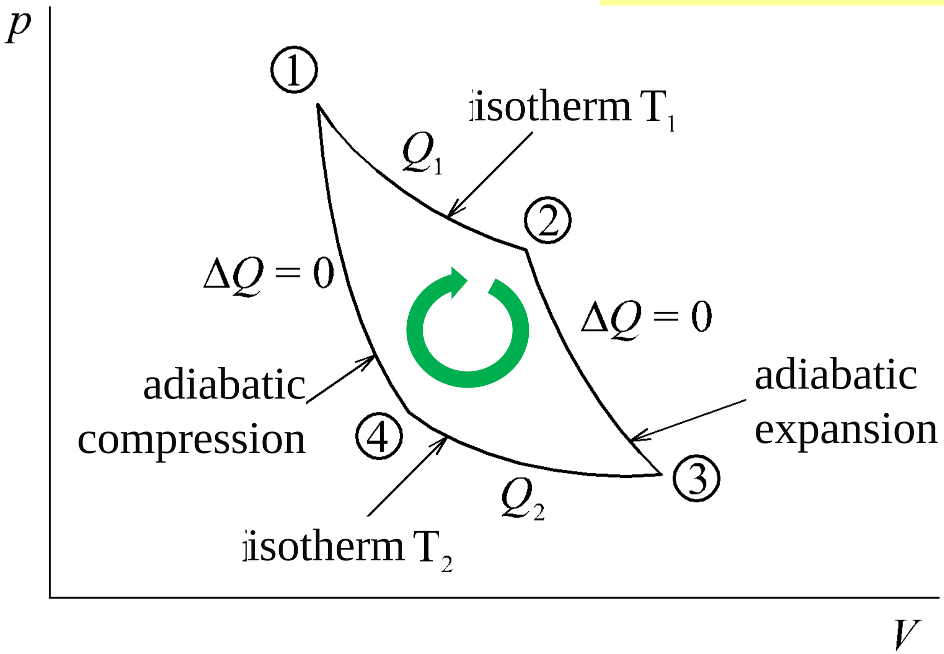
$$W = \binom{N}{n} = \frac{N!}{n!\left(N-n\right)!}$$

Number of microstates that could realize the configuration

Configuration	Left half of the container	Right half of the container	Number of microstates	Microstate probability
$n = 0$		abcd	$W = 1$	**1/16**
$n = 1$	a b c d	bcd acd abd abc	$W = 4$	**4/16**
$n = 2$	ab ac ad bc bd cd	cd bd bc ad ac ab	$W = 6$	**6/16**
$n = 3$	abc abd acd bdc	d c b a	$W = 4$	**4/16**
$n = 4$	abcd		$W = 1$	**1/16**


Number of microstates W
Central
configuration
peak
0
25
50
75
100%
Percentage of molecules in left half

Carnot Engine



$$T_1 V_2^{\kappa-1} = T_2 V_3^{\kappa-1}$$

$$T_2 V_4^{\kappa-1} = T_1 V_1^{\kappa-1}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$Q_1 = A_1 = nR_m T_1 \ln \frac{V_2}{V_1}$$

$$Q_2 = 0$$

$$Q_3 = A_3 = nR_m T_2 \ln \frac{V_4}{V_3}$$

$$Q_4 = 0$$

$$A_2 = -nC_{mV}\left(T_2 - T_1\right) = nC_{mV}\left(T_1 - T_2\right)$$

$$A_4 = -nC_{mV}\left(T_1 - T_2\right) = nC_{mV}\left(T_2 - T_1\right)$$

$$A = A_1 + A_2 + A_3 + A_4 = nR_m T_1 \ln \frac{V_2}{V_1} + nR_m T_2 \ln \frac{V_4}{V_3}$$

$$A = nR_m \left(T_1 \ln \frac{V_2}{V_1} - T_2 \ln \frac{V_3}{V_4} \right) = nR_m \left(T_1 - T_2 \right) \ln \frac{V_2}{V_1}$$

$$\eta = \frac{A}{Q_1}$$

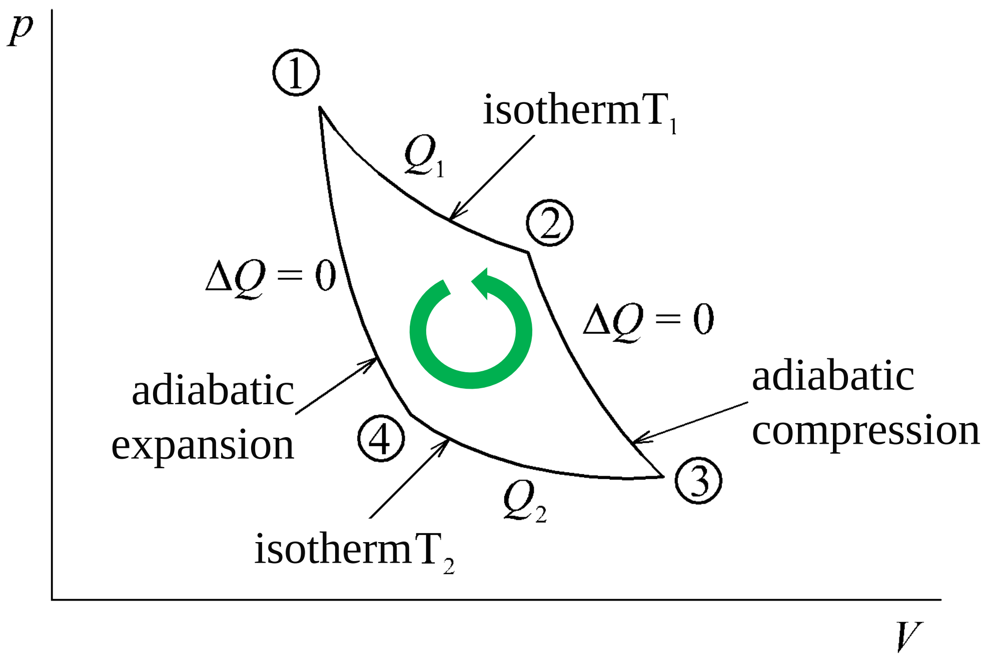
$$\eta = \frac{nR_m \left(T_1 - T_2 \right) \ln \frac{V_2}{V_1}}{nR_m T_1 \ln \frac{V_2}{V_1}}$$

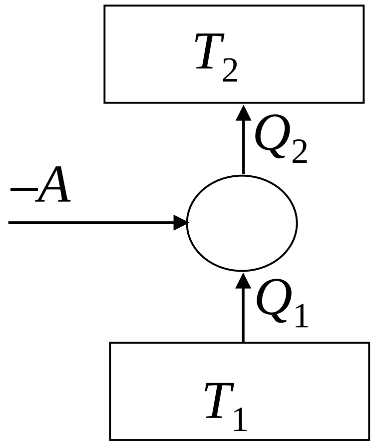
$$\eta = \frac{\left(Q_1 - Q_2 \right)}{Q_1} = \frac{\left(T_1 - T_2 \right)}{T_1}$$

Third law of thermodynamics

It is impossible for any process to reduce the entropy of a system to its absolute-zero value in a finite number of operations.

Refrigerators and Heat pumps





performance coefficient

$$K = \frac{\text{useful heating/cooling}}{\text{work required}}$$

refrigerator $K = \frac{|Q_1|}{|A|} = \frac{|Q_1|}{|Q_2| - |Q_1|} = \frac{T_1}{T_2 - T_1}$ $\qquad K \le 1 \vee K \ge 1$

heat pump $K = \frac{|Q_2|}{|A|} = 1 + \frac{|Q_1|}{|Q_2| - |Q_1|} = \frac{T_2}{T_2 - T_1}$ $\qquad K > 1$

Phase transitions

first-order phase transitions = discontinuous change of density

latent heat L specific latent heat $l = \frac{L}{m}$