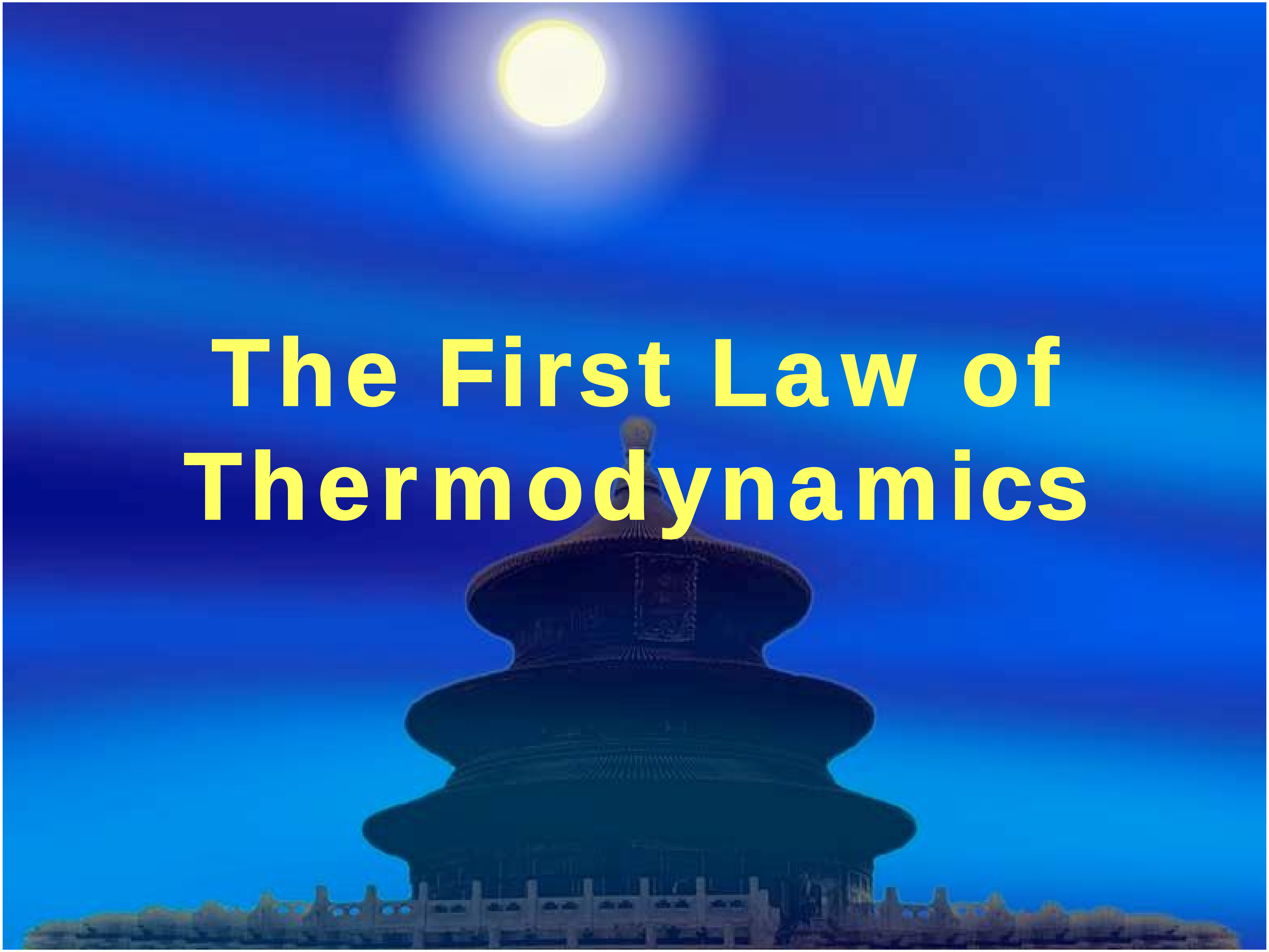
The First Law of Thermodynamics



Work. Internal Energy. And Heat

- **Work**
- In thermodynamics work is defined as energy transfer across the boundary of a system .Work is assigned the symbol **W**.

Kinds of Work:

- The work to vary the volume of a system
- Surface work
- Electrical work
- Magnetic work

- Internal Energy

$$U = U(p,V) = U(p,T) = U(V,T)$$

- The function of states
- Heat
- Energy can be transported across the boundary in two distinct forms: heat and work.
- Energy transported across a boundary as a result of a temperature difference between a system and its surroundings is called heat.

The First Law of Thermodynamics

- The Foundation of The First Law of Thermodynamics
  - The foundation of the law of the conservation of energy
  - determination of the heat equivalence of work
  - Joule experiment

- **Discription:** Whenever a system undergoes a cyclical process, the net quantity of work produced in the surroundings is proportional to the net quantity of heat withdraw from the surroundings, and the constant of proportionality depends only on the units in which work and heat are expressed.

MATHEMATIC EXPRESSION:

$$\Delta U = A + Q$$

$$dU = dA + dQ$$

Quasi-Static Process and Reversible Process

- Process undergoes so slowly that we can think that the process is static;

- States and energy can be completely recovered------reversible process .

Expression to Work

WORK	EXPRESSION
Volume work	$dA = -pdV$ $\quad A = -\int_{V1}^{V2} pdV$
Surface work	$\text{đ}A = \alpha ds$
Electrical work	$\text{đ}A = V\vec{E} \cdot d\vec{P}$
Magnetic work	$\text{đ}A = \mu_0 V \vec{H} \cdot d\vec{M}$
Universal work	$\text{đ}A = \sum_i Y_i dy_i$

Heat Capacity and Enthalpy

- 1.constant-volume heat capacity and specific heat, mole heat capacity:

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

$$c_V = \frac{1}{M}\left(\frac{\partial U}{\partial T}\right)_V$$

$$C_{m,V} = \left(\frac{\partial U_m}{\partial T}\right)_V \qquad U_m = \frac{\mu}{M}U$$

- 2.constant-pressure heat capacity and specific heat, mole heat capacity:
  - **Enthalpy:** $H = U + pV$

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

$$c_p = \frac{1}{M}\left(\frac{\partial H}{\partial T}\right)_p$$

$$C_{m,p} = \left(\frac{\partial H_m}{\partial T}\right)_p \qquad H_m = \frac{\mu}{M} H$$

- 3.The relationship between Cv and Cp:

$$C_p - C_V = \nu R$$

$$C_{mp} - C_{mV} = R$$

$$Let\ \gamma = \frac{C_p}{C_V} \Rightarrow C_V = \frac{\nu R}{\gamma - 1},\ C_p = \frac{\gamma \nu R}{\gamma - 1}$$

γ is adiabatic coefficient

Internal Energy of Gas

- 1. Joule experiment
  - Adiabatic, free expansion→ Q=0, A=0
  - No temperature change →DT=0
- 2. **Analyze to** Joule experiment :

Let $\Delta U = \left(\frac{\partial U}{\partial V}\right)_T \Delta V + \left(\frac{\partial U}{\partial T}\right)_V \Delta T$

For $\Delta U = A + Q$

In Joule experiment $A = 0, Q = 0, \therefore \Delta U = 0$

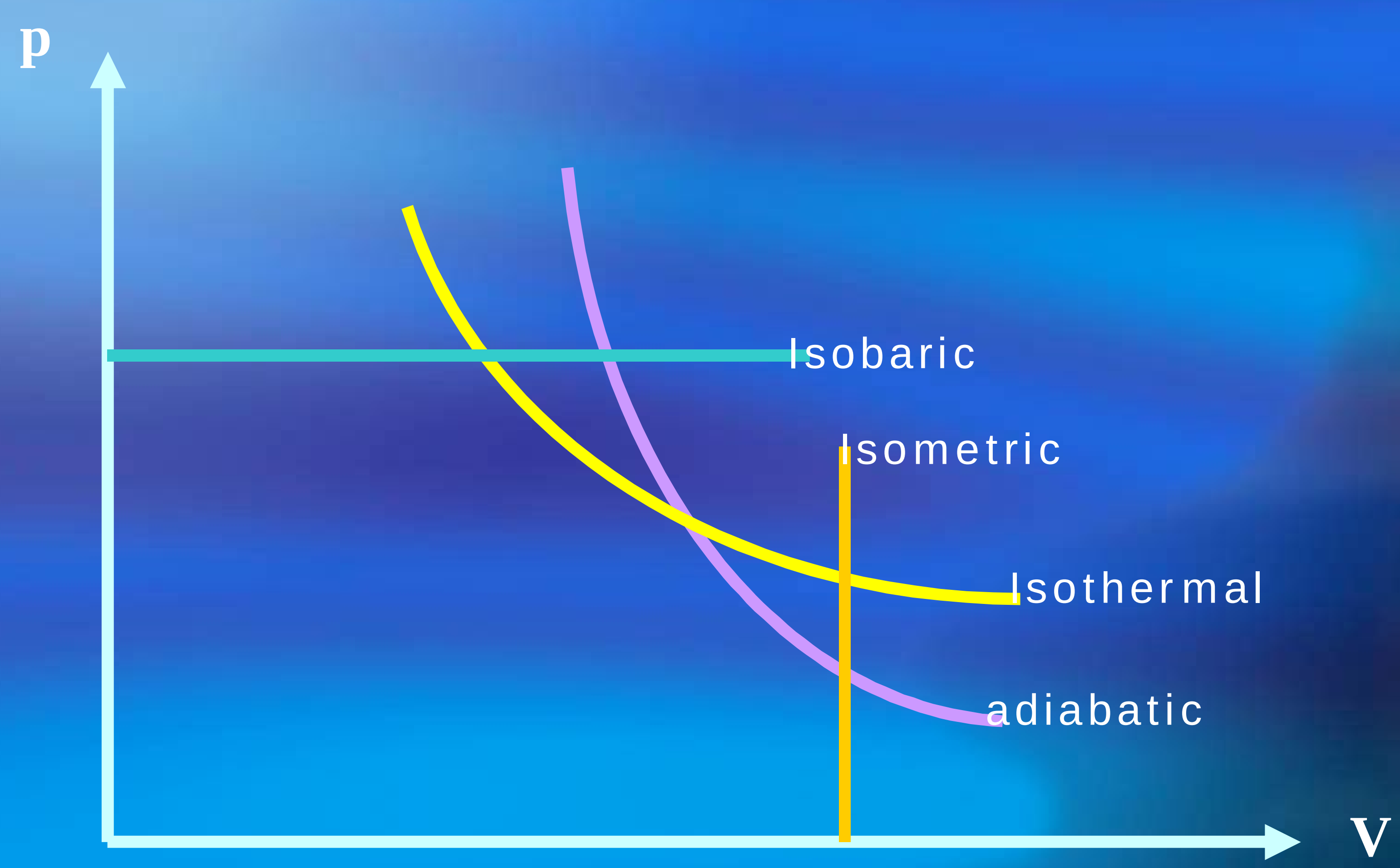
The result of the experiment $\Delta T = 0$,

So $\Delta U = 0 = \left(\frac{\partial U}{\partial V}\right)_T \Delta V \Rightarrow U = U(T)$.

Thermodynamic Processes of the Ideal Gas

- 1.Isometric Process, V=C
- 2.Isobaric Process, P=C
- 3.Isothermal Process, T=C
- 4.Adiabatic Process, Q=0
- 5.Polytropic Process

The graph of these processes:



The main formula of these processes:

	EQUATION	W	Q	ΔU	C
1	$V = C$ or $\frac{p}{T} = C'$	0	$\nu C_{m,V}(T_f - T_i)$	$\nu C_{m,V}(T_f - T_i)$	$C_{m,V}$
2	$p = C$ or $\frac{V}{T} = C'$	$-p(V_f - V_i)$ or $-\nu R(T_f - T_i)$	$\nu C_{m,p}(T_f - T_i)$	$\nu C_{m,V}(T_f - T_i)$	$C_{m,p}$
3	$pV = C$	$-p_i V_i \ln V_f / V_i$ or $-\nu RT_i \ln V_f / V_i$	$-A$	0	$\pm\infty$

	EQUATION	W	Q	ΔU	C
4	$pV^{\gamma}=C1$ $V^{\gamma-1}T=C2$ $p^{\gamma-1}/T^{\gamma}=C3$	$\frac{1}{\gamma-1}(p_fV_f-p_iV_i)$	0	$\nu C_{m,V}(T_f-T_i)$	0
5	$pV^{n}=C1$ $V^{n-1}T=C2$ $p^{n-1}/T^{n}=C3$	$\frac{1}{n-1}(p_fV_f-p_iV_i)$	$\nu C_{m,n}(T_f-T_i)$ $(n\neq1)$	$\nu C_{m,V}(T_f-T_i)$	$C_{m,n}=C_{m,V}\left(\frac{\gamma-n}{1-n}\right)$

Cycle Process

- 1.Cycle process and its efficiency:

$$A = Q_1 - Q_2$$

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

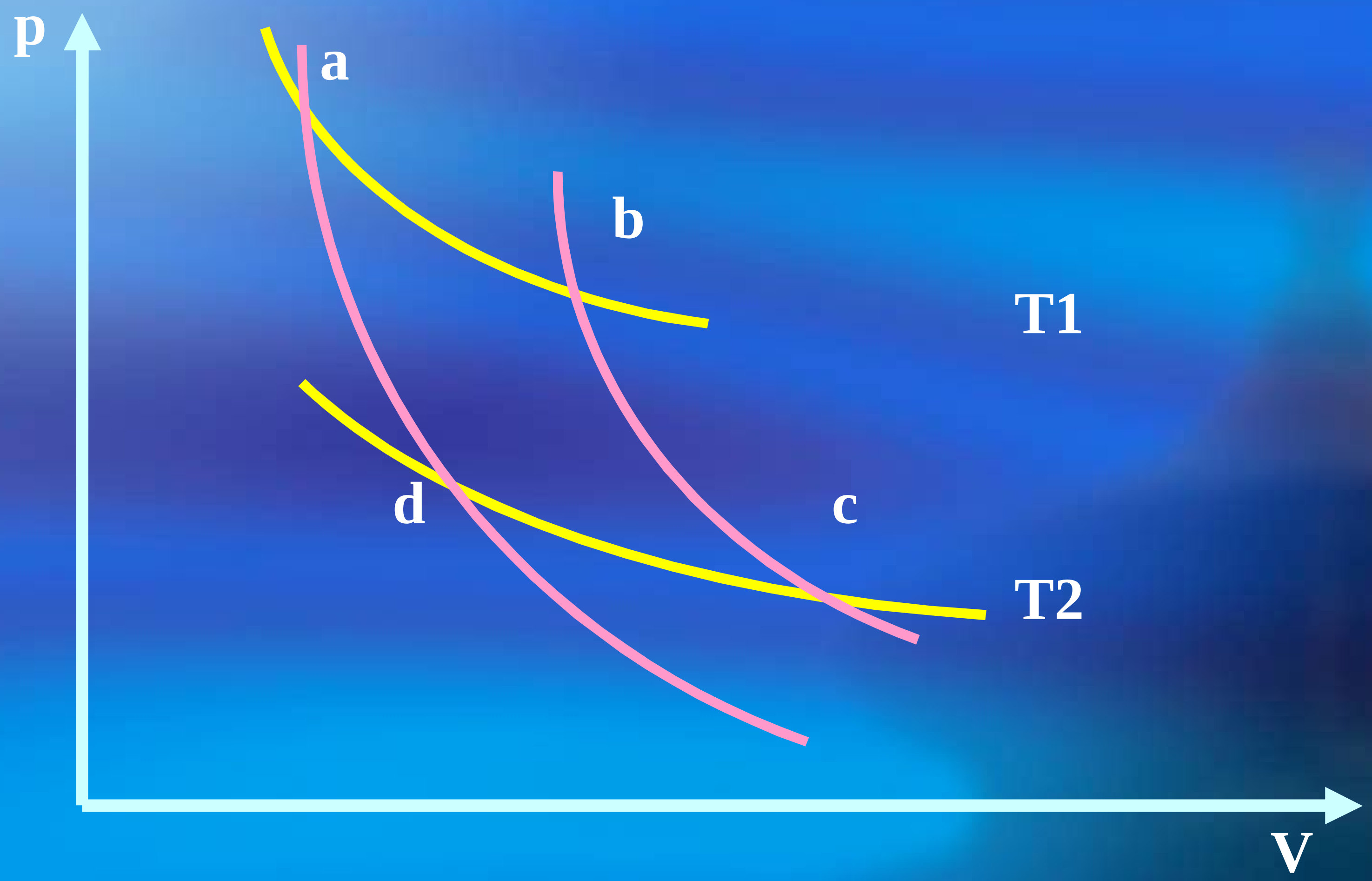
- 2.Heat engine cycle:

$$\varepsilon_p = \frac{Q_h}{A}$$

- 3.Refrigerator cycle:

$$\varepsilon_r = \frac{Q_2}{A} = \frac{Q_2}{Q_1 - Q_2}$$

4.Carnot cycle：



- The efficiency of the Carnot cycle:

$$Q_1 = RT_1 \ln\frac{V_b}{V_a}$$

$$Q_2 = RT_2 \ln\frac{V_c}{V_d}$$

$$\text{for } \frac{V_c}{V_b} = \frac{V_d}{V_a} \Rightarrow \ln\frac{V_c}{V_d} = \ln\frac{V_b}{V_a}$$

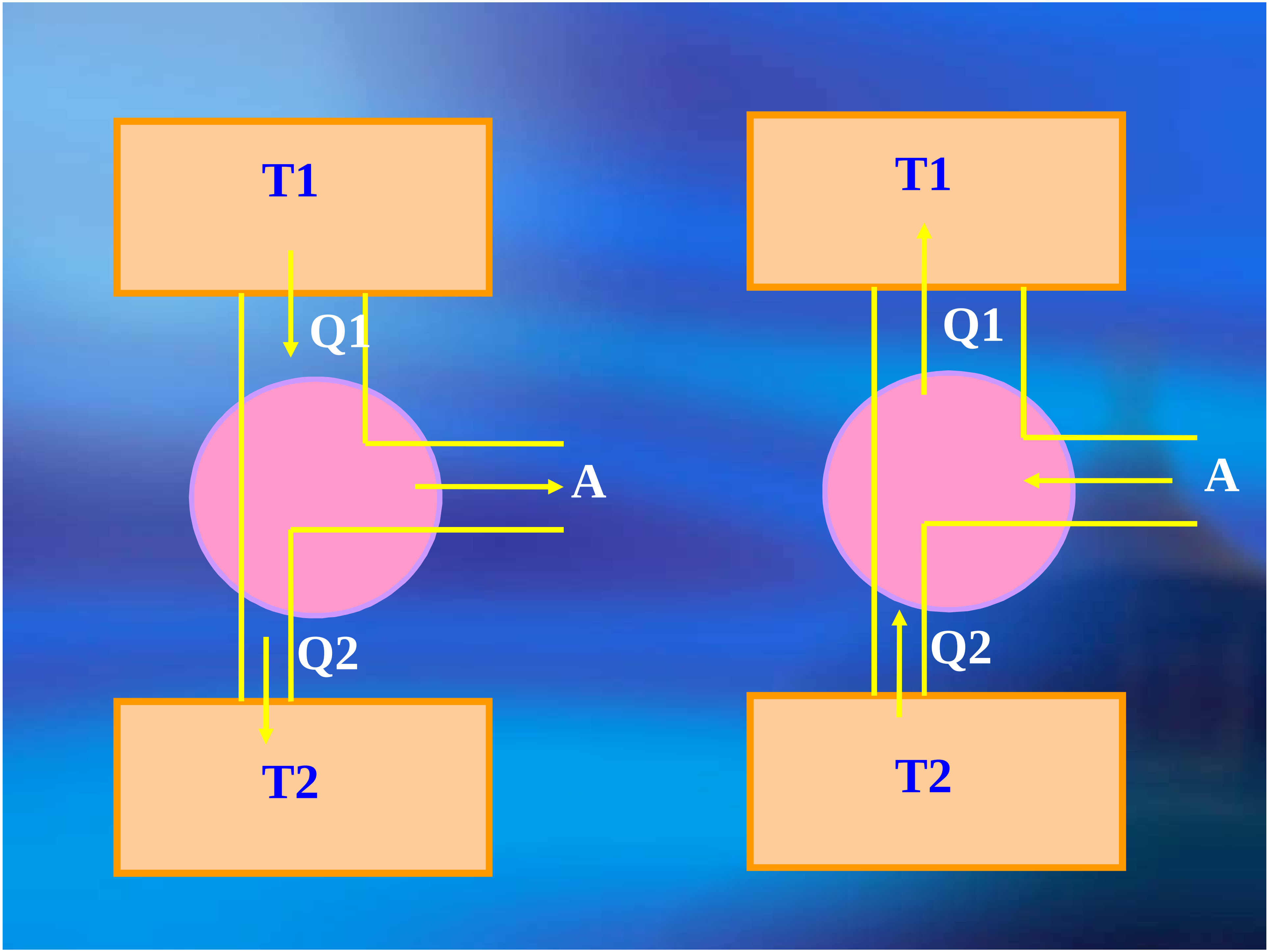
$$\text{so } \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

- Refrigeration-efficiency in Carnot cycle:

$$\varepsilon_r = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

- Heat engine-efficiency in Carnot cycle:

$$\varepsilon_p = \frac{Q_1}{A} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$


T1
Q1
A
Q2
T2
T1
Q1
A
Q2
T2