Specific Heat and Calorimetry; Heat engine overview

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Outline

1. Specific heat and calorimetry
2. Specific heat of ideal gas
3. Heat engine overview

1. Specific heat and calorimetry

Specific heat and molar specific heat

- The heat it takes to raise the temperature of 1 kg of a given substance by 1 K is called the **specific heat** c of that substance. In equation:

$$Q = Mc\Delta T$$

- Similarly, the heat it takes to raise the temperature of 1 mole of a substance by 1 K is its **molar specific heat** C. In equation:

$$Q = nC\Delta T$$

Specific heat: units and conventions

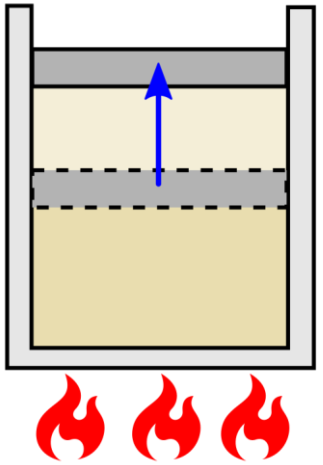
- The SI unit for specific heat is J/kg·K
- The SI unit for molar specific heat is J/mol·K
- Since specific heat is concerned only with change in temperature, there is no real difference between measurement in °C and K

Specific heat and thermal energy

- Since **solids** and **liquids** are essentially incompressible, we may assume $W = 0$ when they are heated or cooled. By the first law of thermodynamics, we thus have:

$$\Delta E_{\text{th}} = Q = Mc\Delta T$$

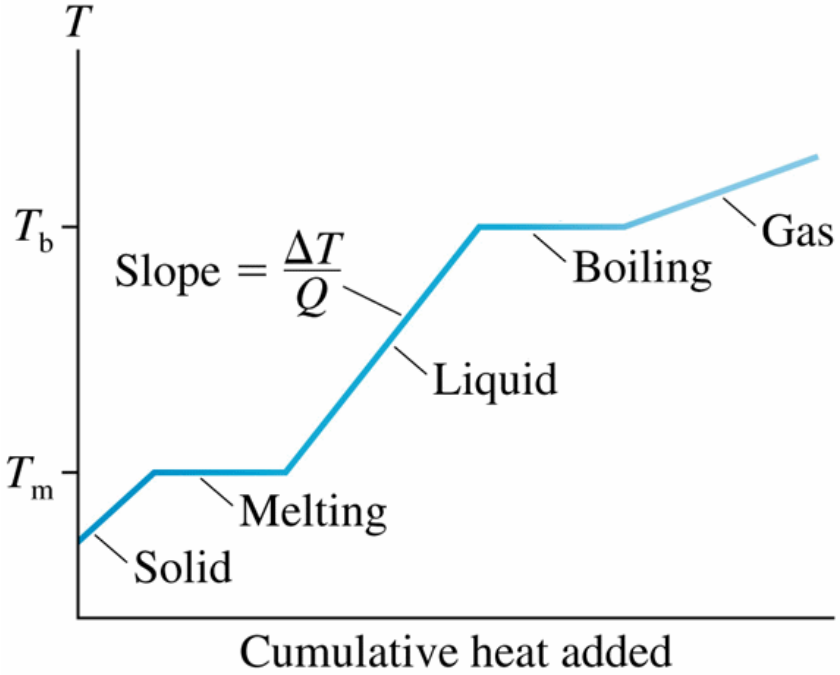
- In contrast, a gas expands when heated under constant pressure, which turns out to contribute $W < 0$. As a result, we generally have $c_P > c_V$ in a gas

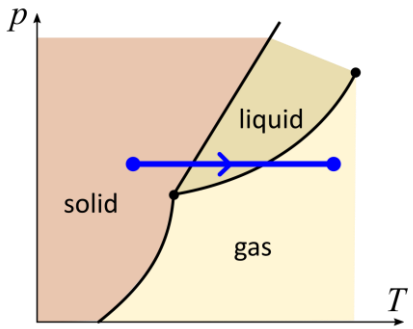


Heat of transformation

- When a substance is undergoing phase change, additional energy is needed to reorganize its microscopic structure
- The **heat of transformation** L is the additional heat needed for this process for each 1 kg of the substance. In equation:

$$Q = ML$$





Heat of transformation: signs and conventions

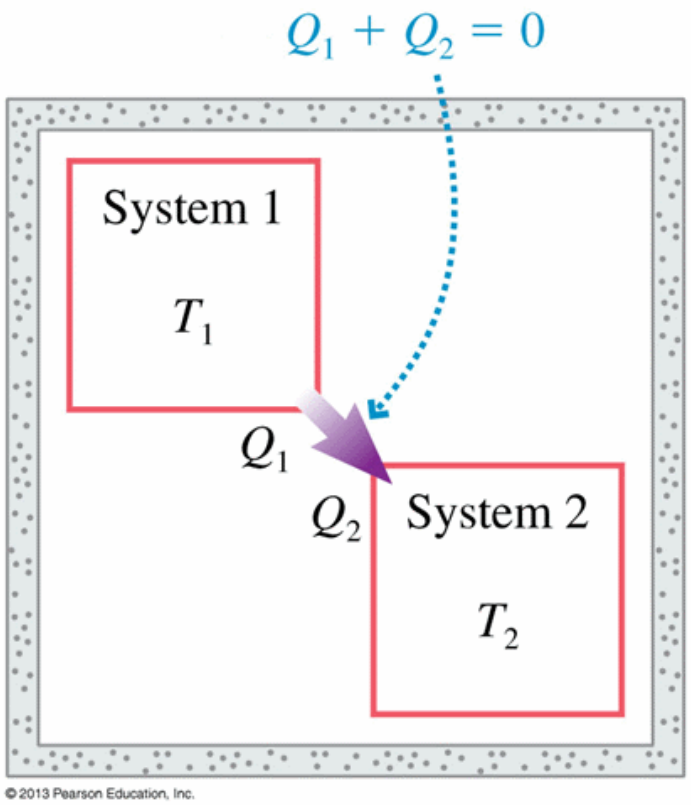
- Heat of transformation is also known as **latent heat**
- The SI unit for heat of transformation is is J/kg
- In general, L is different for different phase change. Also, note the sign reverse between heating and cooling. Thus,

$$Q = \pm ML_f \qquad \text{(+ melt / − freeze)}$$

$$Q = \pm ML_v \qquad \text{(+ boil / − condense)}$$

Calorimetry

- When two objects are in thermal contact with each other but isolated from everything else, we must have $|Q_1| = |Q_2|$
- Regardless of the initial temperatures, when thermal equilibrium is reached we must have $T_1 = T_2$



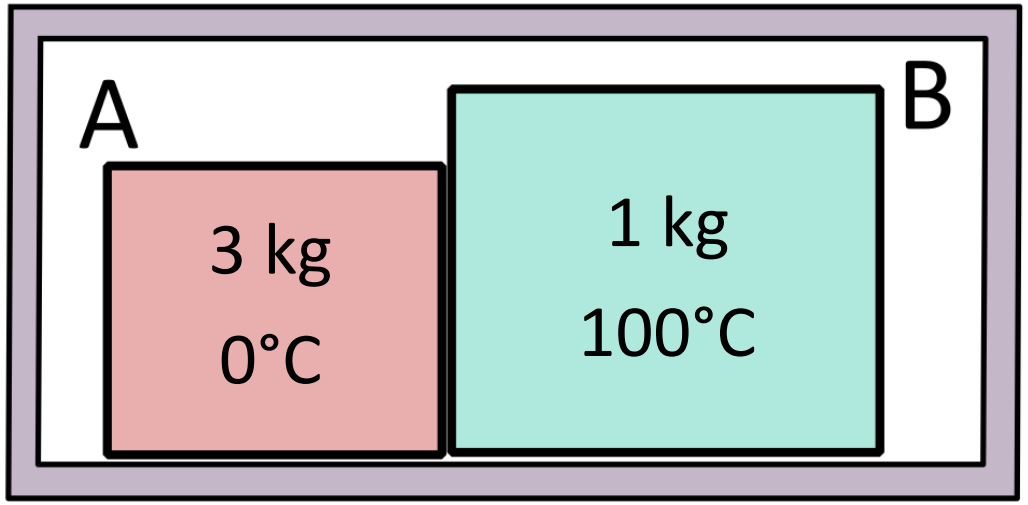
Your turn: heat capacity and heat exchange

Two objects A and B are brought into thermal contact with each other but are otherwise well-isolated from the surrounding. If $c_B = 2c_A$, the final (equilibrium) temperature is:

A. $T_f < 50°C$

B. $T_f = 50°C$

C. $T_f > 50°C$



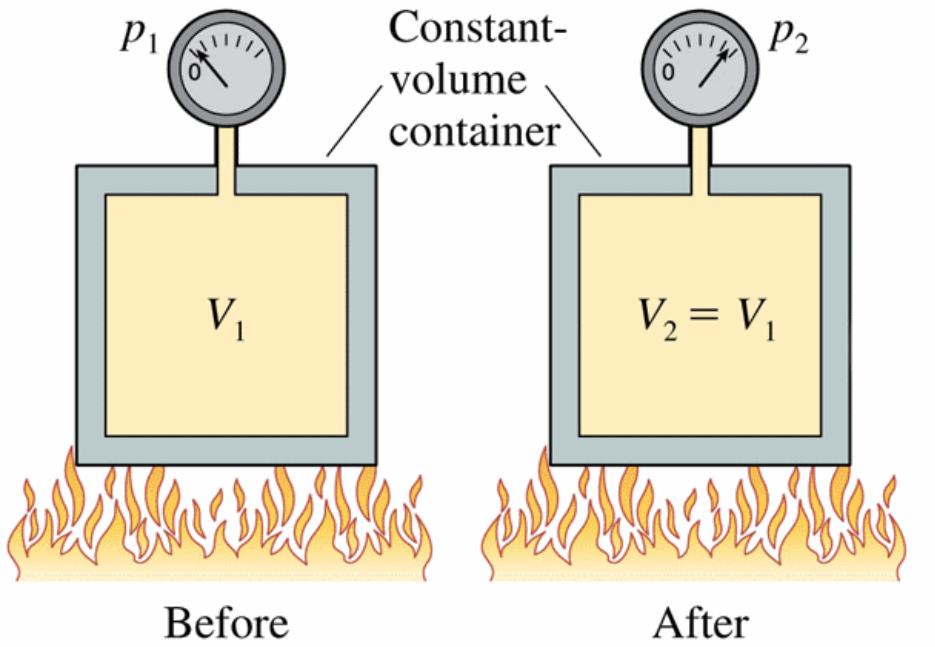
Numerical practice: calorimetry

A 750 g aluminum pan ($c = 900$ J/kg·K) are removed from the stove and plunged into a sink filled with 10.0 L of water ($c = 4190$ J/kg·K) at 20°C. The water temperature quickly rises before it stabilizes at 24.0°C. What was the initial temperature of the pan in °C?

2. Specific heat of ideal gas

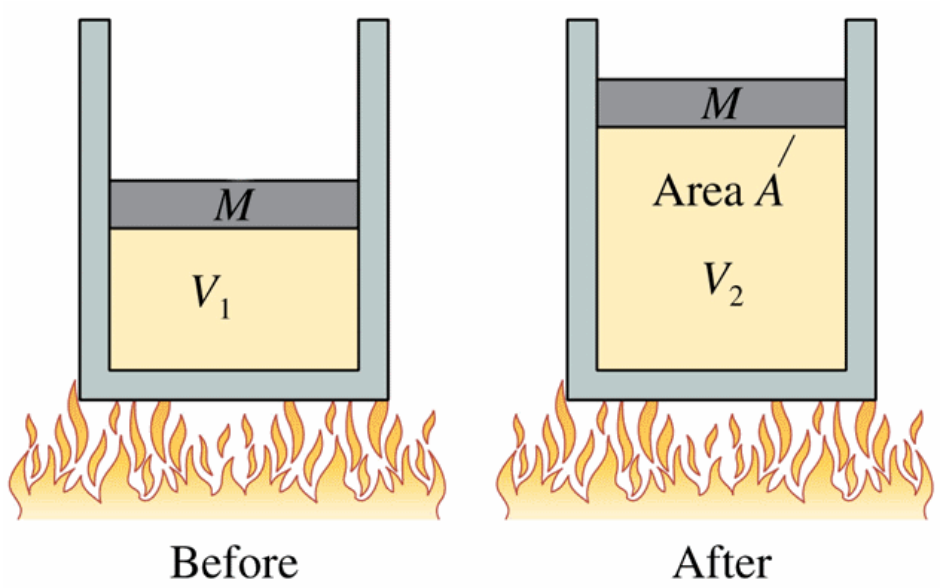
Reminder: isochoric vs isobaric processes

- Isochoric (V = const.) process:



$$Q = \Delta E_{\text{th}} = \frac{3}{2} nR\Delta T$$

- Isobaric (p = const.) process:



$$Q = \Delta E_{\text{th}} - W = \frac{5}{2} nR\Delta T$$

Molar specific heat for monoatomic ideal gas

- Recall the definition of molar specific heat C: $Q = nC\Delta T$

- For constant volume process,

$$Q = \Delta E_{\text{th}} = \frac{3}{2} nR\Delta T$$

- Thus (for monoatomic gas)…

$$C_V = \frac{3}{2} R$$

- For constant pressure process,

$$Q = \Delta E_{\text{th}} = \frac{5}{2} nR\Delta T$$

- Thus (for monoatomic gas)…

$$C_P = \frac{5}{2} R$$

Relationship between C_P and C_V

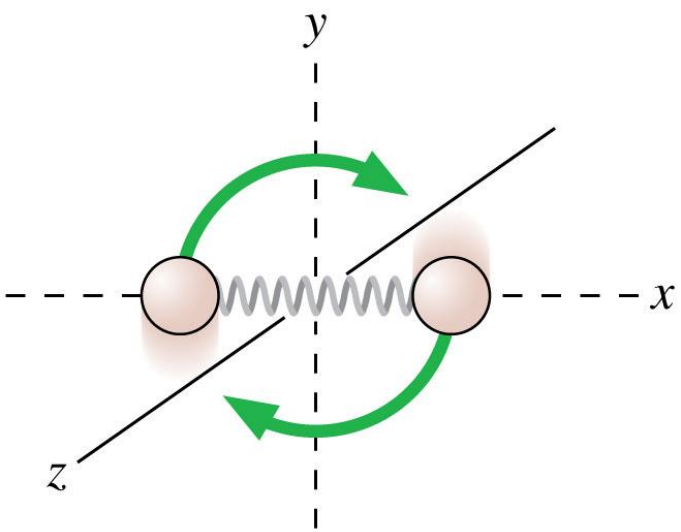
- From $C_V = \frac{3}{2}R$ and $C_P = \frac{5}{2}R$, we see that $C_P = C_V + R$
- This difference stems from the work done in the constant pressure case, where in $W = -p\Delta V = -nR\Delta T$
- Note that no monoatomic assumption is made. So in general:

$$\boxed{C_P = C_V + R}$$

(**all** ideal gas)

Beyond monoatomic gas: new degrees of freedom

- In addition to an overall translational motion, diatomic molecule can rotate about 2 of its axes and can vibrate about its bond axis



Rotation end-over-end about the z-axis

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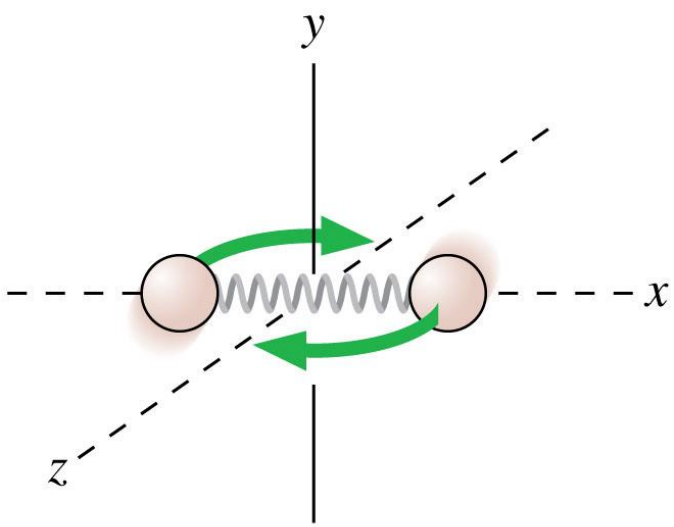

Rotation end-over-end about the y-axis

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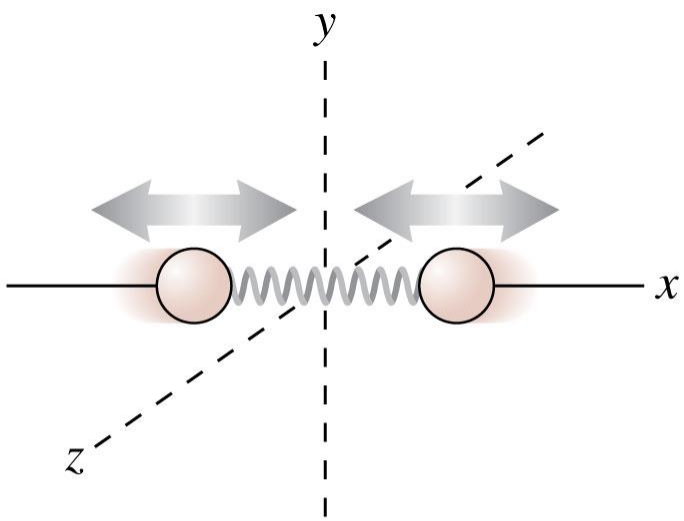

Vibration back and forth along the x-axis

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Beyond monoatomic gas: counting degrees of freedom

- Each additional "degree of freedom" can store energy and thus contributes additionally to E_{th} and hence C_{V}
- For diatomic molecule, the counting goes:

$$3 \text{ translation} + 2 \text{ rotation} + \underbrace{2 \text{ vibration}}_{1 \text{ potential} + 1 \text{ kinetic}} = 7 \text{ degrees of freedom}$$

- For translation, we get $\frac{1}{2}k_B T$ per degree of freedom per molecule, how about the other new degrees of freedom?

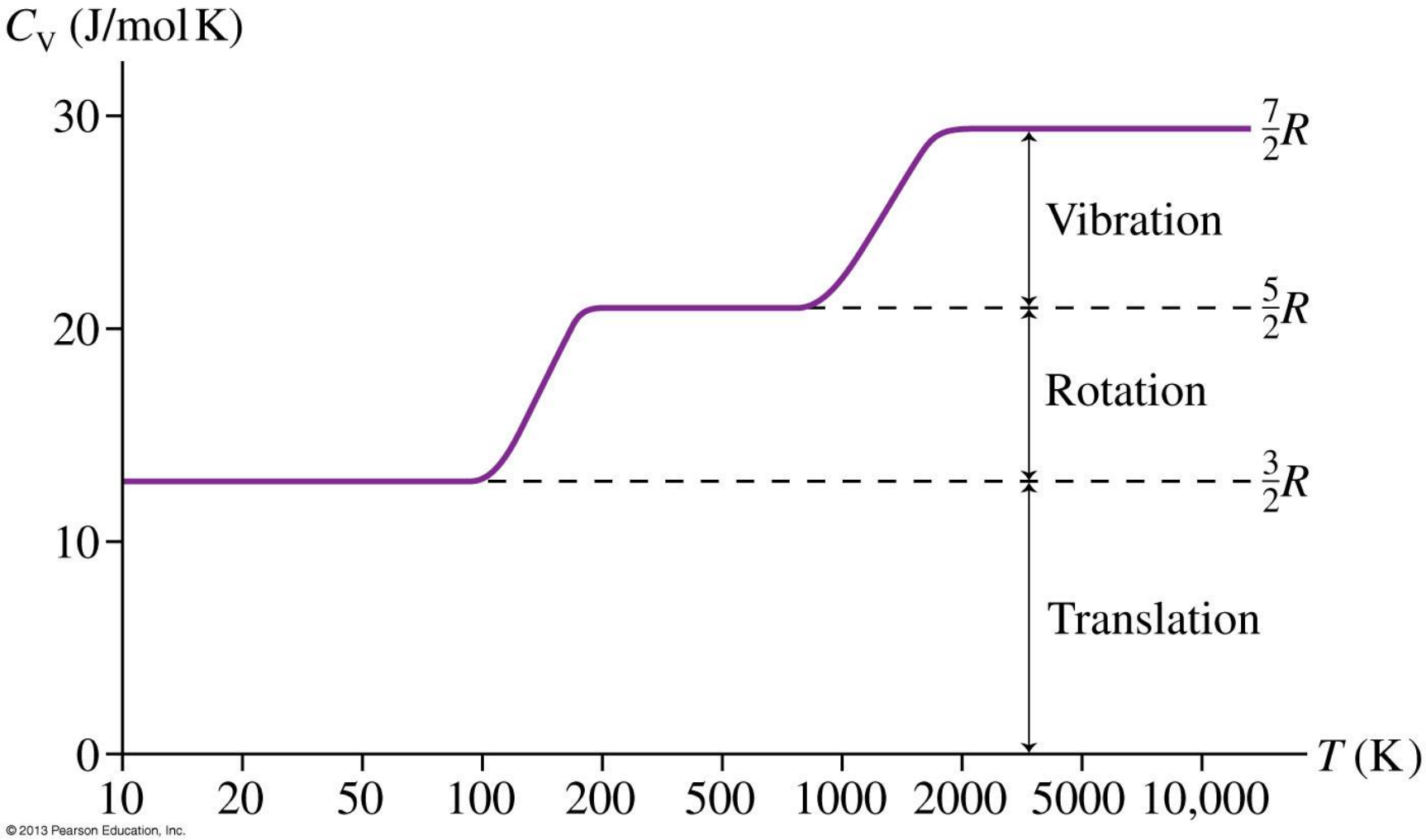
Beyond monoatomic gas: the equipartition theorem

- The **equipartition theorem** from *classical* statistical mechanics says:

> The thermal energy of a system of particles is equally divided among all degrees of freedom. More specifically, the energy stored in each degree of freedom is $\frac{1}{2}k_B T$ per particle

- However, because of *quantum* mechanics, the contributions from rotation and vibration are "activated" only at higher temperatures

Beyond the monoatomic gas: putting all together



Upshot: use $C_V = \frac{5}{2}R$ for diatomic gas at "typical" temperatures $200\text{ K} \lesssim T \lesssim 800\text{K}$

Your turn: counting degrees of freedom

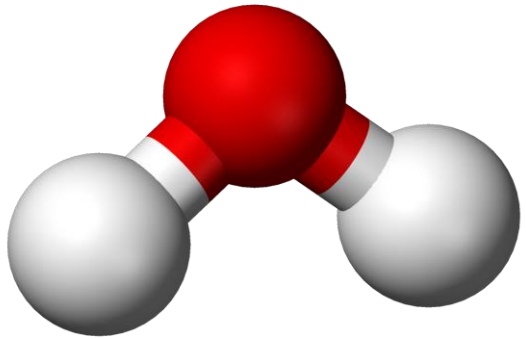
Consider the water molecule (see figure). How many **rotational** degrees of freedom does it has?

A. 2 degrees of freedom

B. 3 degrees of freedom

C. 4 degrees of freedom

D. 6 degrees of freedom



3. Heat engine overview

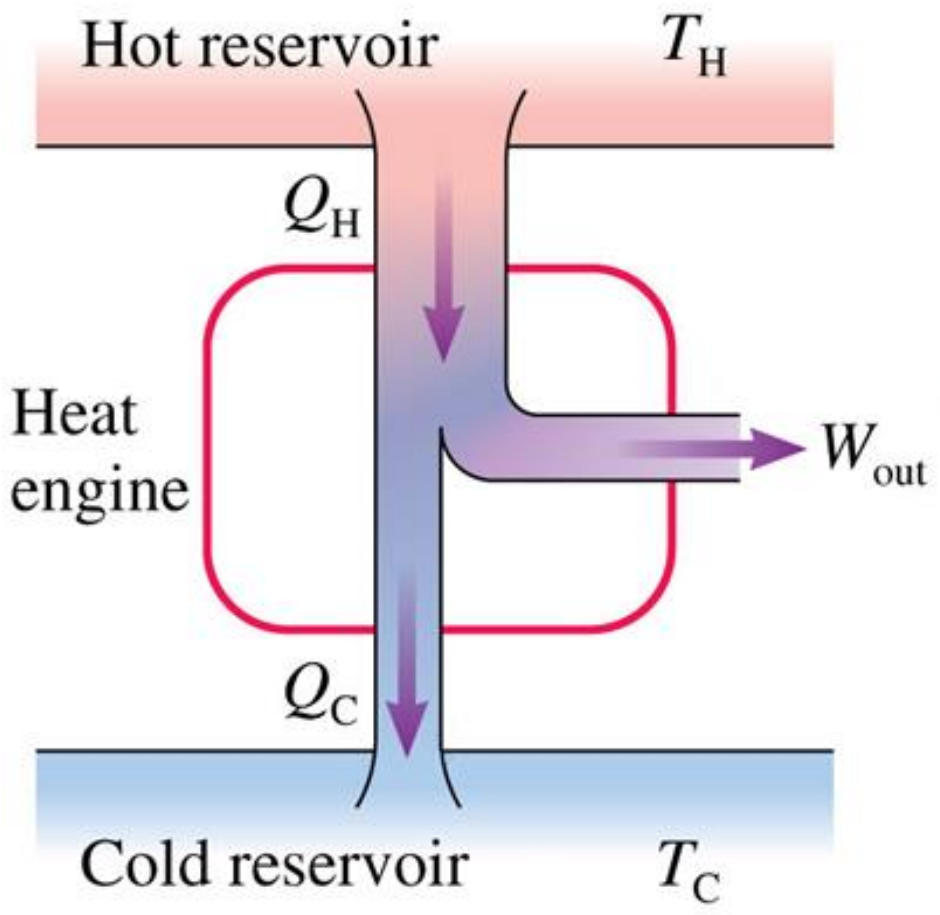
Basic properties of a heat engine

- **Heat engine** converts heat into useful work
- Conceptually, car engines, steam generators, etc. are all heat engine of some kind
- A heat engine operates in **cycles**, i.e., it returns to its initial state periodically
- A heat engine general operates between a **hot reservoir** and a **cold reservoir**

Energy-transfer diagram and relevant quantities

- T_H = temperature of hot reservoir
- T_C = temperature of cold reservoir
- Q_H = heat absorbed from hot reservoir
- Q_C = heat released to cold reservoir
- W_{out} = useful work output

*Q_H, Q_C, and W_{out} are values **per cycle**, and are all taken to be **positive**



First law of thermodynamics on heat engine

- Relating our definitions,

$$Q = Q_H - Q_C$$

$$W = -W_{\text{out}}$$

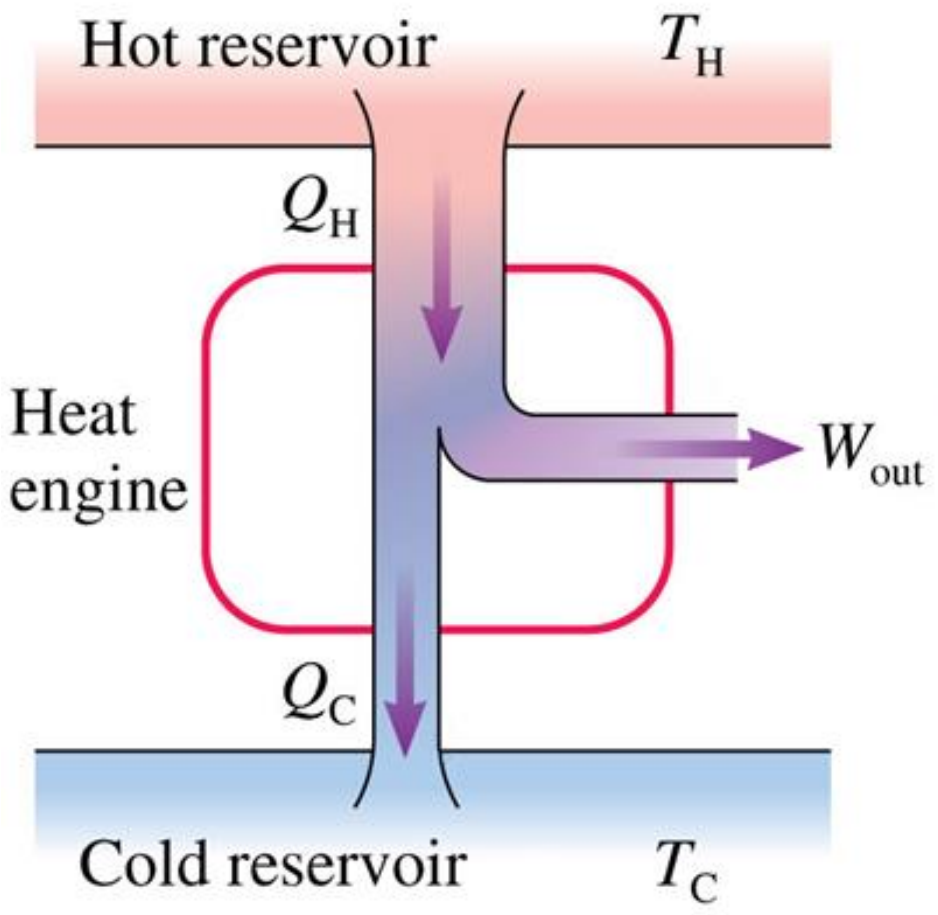
(per cycle)

- Since the heat engine is cyclic,

$\Delta E_{\text{th}} = 0$ after each cycle

- Thus, 1st law implies:

$$\boxed{W_{\text{out}} = Q_H - Q_C}$$

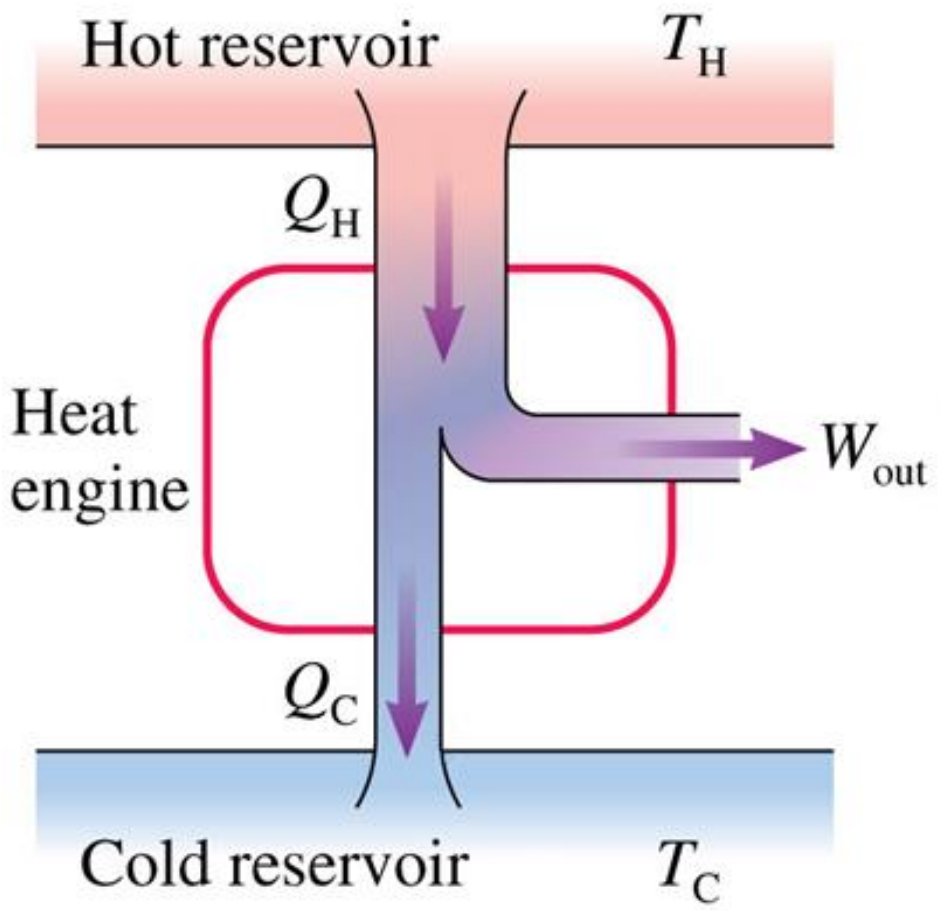


Heat engine efficiency

- The **thermal efficiency** of a heat engine, η, is defined as:

$$\eta = \frac{W_{\text{out}}}{Q_H}$$

- One important question for heat engine is whether η is limited

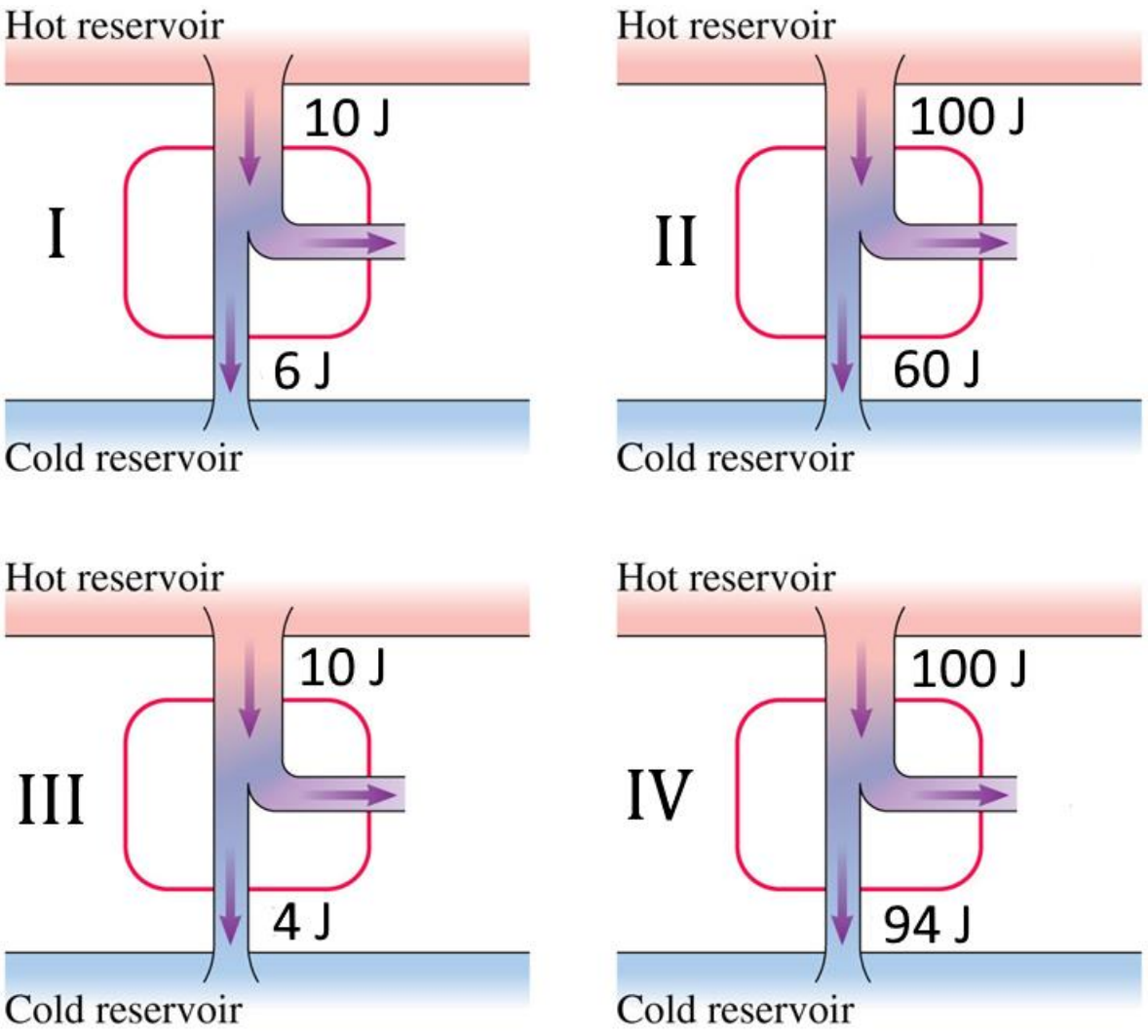


Your turn: heat engine efficiency

Rank the following heat engines by thermal efficiency, from largest to smallest

A. (II) > (III) = (IV) > (I)

B. (II) = (IV) > (I) = (III)

C. (III) > (I) = (II) > (IV)

D. (IV) > (II) > (I) > (III)