7 Heat and Enthalpy

A metal bench and a wooden bench that sat outside all night are at the same temperature, yet the metal one feels colder. Your hand is not reading temperature; it is reading how fast heat leaves you. That is the habit this chapter builds: heat is something that moves, it always moves from one thing to another, and every question turns on which direction it went and whose it was. The mock exam gives this chapter 8 of its 70 questions.

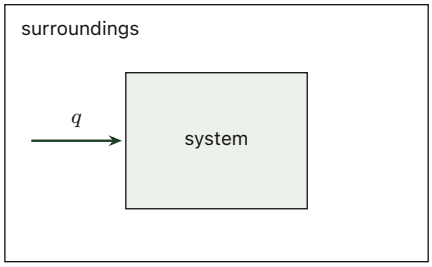
7.1 System and Surroundings

Energy changes are tracked by choosing a part of the universe to follow. That part is the **system**. Everything else is the **surroundings**: the flask, the water, the air. **Heat**, q, is energy that moves between them because of a temperature difference.

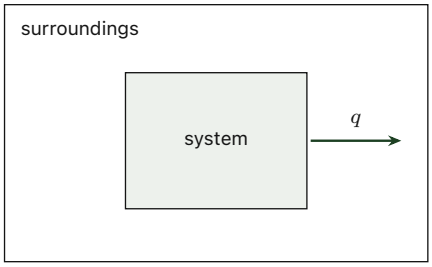
System
The part of the universe you follow, such as the reacting mixture.

Every sign in this chapter is written from the system's point of view. A positive value means energy enters the system. A negative value means energy leaves it. Energy is conserved, so what one side gains the other side loses:

$$q_{\text{sys}} = -q_{\text{surr}}$$



endothermic
$q_{\text{sys}} > 0 \quad q_{\text{surr}} < 0$



exothermic
$q_{\text{sys}} < 0 \quad q_{\text{surr}} > 0$

A process that absorbs heat is **endothermic**. A process that releases heat is **exothermic**. Breaking attractions or bonds absorbs energy, and forming them releases it.

Endothermic, exothermic
Endothermic: $q_{\text{sys}} > 0$ and the surroundings cool. Exothermic: $q_{\text{sys}} < 0$ and they warm.

Endothermic	Exothermic
melting, vaporizing, sublimation	freezing, condensation, deposition
dissolving NH_4NO_3 in water	combustion
breaking bonds	forming bonds

Which object is the system?

The same event has opposite signs for the two objects, so the choice of system sets the sign. In a calorimeter the reaction is the system and the solution is the surroundings. If the solution gets warmer, then $q_{\text{solution}} > 0$ and $q_{\text{rxn}} < 0$.

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RULE Name the object before writing a sign. $q_{\text{rxn}} = -q_{\text{solution}}$.

7.2 Internal Energy, Work, and the First Law

The **internal energy**, E, of a system is the total kinetic and potential energy of its particles. Its absolute value cannot be measured, but its change can. E is a **state function**. The **first law of thermodynamics** says that energy is conserved:

$$\Delta E = q + w$$

State function
A quantity set only by the current state of the system, not by how it got there.

Here w is **work**, energy transferred when a force moves something through a distance. For a gas, work is done when the gas expands or is compressed. The values of q and w depend on the path taken. Their sum does not.

	Positive	Negative
q	heat absorbed by the system	heat released by the system
w	work done on the system (compression)	work done by the system (expansion)

Gas work at constant external pressure is

$$w = -P_{\text{ext}}\,\Delta V$$

A gas that expands has $\Delta V > 0$, so $w < 0$. The system loses energy. A gas that is compressed has $\Delta V < 0$, so $w > 0$. With pressure in atm and volume in L the product has units of L·atm, which must be converted to joules:

$$1\ \text{L}\cdot\text{atm} = 101.3\ \text{J}$$

Constant volume and constant pressure

At constant volume, $\Delta V = 0$, so $w = 0$ and $\Delta E = q$. At constant pressure the heat is the enthalpy change, $q_P = \Delta H$. Section 7.5 develops this.

EXAMPLE 7.1

A gas is compressed. The surroundings do 38 J of work on it, and it releases 74 J of heat. What is ΔE for the gas?

What is asked ΔE of the gas, so the gas is the system.

Heat Released by the system, so $q = -74$ J.

Work Done on the system, so $w = +38$ J.

Add $\Delta E = q + w = -74\ \text{J} + 38\ \text{J} = -36\ \text{J}$

Check More energy left as heat than entered as work, so ΔE is negative.

Answer $\Delta E = -36$ **J**

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EXAMPLE 7.2

A gas absorbs 1.25 kJ of heat and expands from 2.00 L to 6.50 L against a constant external pressure of 0.800 atm. What is ΔE?

What is asked	ΔE of the gas, in kJ.
Heat	Absorbed, so $q = +1.25$ kJ.
Volume change	$\Delta V = 6.50 - 2.00 = +4.50$ L
Work	$w = -P\Delta V = -(0.800\ \text{atm})(4.50\ \text{L}) = -3.60\ \text{L}\cdot\text{atm}$
Convert	$-3.60\ \text{L}\cdot\text{atm} \times 101.3\ \text{J}/(\text{L}\cdot\text{atm}) = -365\ \text{J} = -0.365\ \text{kJ}$
Add	$\Delta E = 1.25 + (-0.365) = +0.885$ kJ
Check	The gas expanded, so work left the system and ΔE is smaller than q.
Answer	$\Delta E = +0.885$ **kJ**

7.3 Heat Capacity and Thermal Equilibrium

Heat capacity
Heat needed to raise an object's temperature by 1 °C. Units: J/°C.

The temperature change of an object depends on the heat it receives and on its **heat capacity**, C. The **specific heat**, c, is the heat capacity of one gram: the heat needed to raise 1 g by 1 °C. A sample of mass m has $C = mc$.

$$q = mc\,\Delta T \qquad \Delta T = T_{\text{final}} - T_{\text{initial}}$$

The sign of q follows the sign of ΔT. A sample that warms has $q > 0$. A change of 1 °C equals a change of 1 K, so c may be written in J/(g·°C) or J/(g·K).

Substance	water	ethanol	aluminum	iron	copper	lead
c, J/(g·°C)	4.184	2.44	0.897	0.449	0.385	0.129

A small specific heat means the temperature changes easily. For the same heat and the same mass, lead warms far more than water does.

Thermal equilibrium

Two objects at different temperatures in an insulated container exchange heat until they reach one final temperature. No heat leaves the container, so the two objects together have no net heat change:

$$q_{\text{hot}} + q_{\text{cold}} = 0$$

Write each q as $mc\,\Delta T$, with $\Delta T = T_f - T_i$ for that object. The hot object comes out negative on its own. Then solve for the one unknown.

$$m_1 c_1 (T_f - T_1) + m_2 c_2 (T_f - T_2) = 0$$

RULE Each q uses its own object's mass, specific heat and ΔT. Never share one ΔT.

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PRACTICE SET 7A 12 questions · 18 minutes · signs, work and the first law

1. Solid ammonium nitrate dissolves in water in a beaker, and the beaker feels cold. Taking the dissolving process as the system, which statement is correct?

(A) $q_{\text{sys}} < 0$, and the process is exothermic
(B) $q_{\text{sys}} > 0$, and $q_{\text{surr}} < 0$
(C) $q_{\text{sys}} > 0$, and the surroundings gain heat
(D) $q_{\text{sys}} < 0$, and $q_{\text{surr}} < 0$

2. A gas absorbs 340 J of heat and does 125 J of work on its surroundings. What is ΔE for the gas?

(A) -465 J **(B)** -215 J
(C) $+465$ J **(D)** $+215$ J

3. A gas expands from 1.50 L to 5.00 L against a constant external pressure of 1.50 atm. What is the work w for the gas?

(A) -532 J **(B)** $+532$ J
(C) -5.25 J **(D)** -0.0518 J

4. A reaction warms 150 g of solution in a coffee-cup calorimeter by 4.0 °C. Take $c = 4.184$ J/(g·°C) for the solution. What is q for the reaction?

(A) $+2.51$ kJ **(B)** -2.51 kJ
(C) -0.60 kJ **(D)** $+0.60$ kJ

5. A hot metal sample is dropped into cool water in an insulated cup, and both reach one final temperature. Which pair gives the signs of q for the metal and for the water?

(A) $q_{\text{metal}} > 0,\ q_{\text{water}} < 0$ **(B)** $q_{\text{metal}} > 0,\ q_{\text{water}} > 0$
(C) $q_{\text{metal}} < 0,\ q_{\text{water}} < 0$ **(D)** $q_{\text{metal}} < 0,\ q_{\text{water}} > 0$

6. For a system, $\Delta E = -150$ J and $w = +90$ J. What is q?

(A) -60 J **(B)** $+60$ J
(C) -240 J **(D)** $+240$ J

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