



CHEM2100J Chemistry Autumn 2024

Chapter 07 The First Law of Thermodynamics

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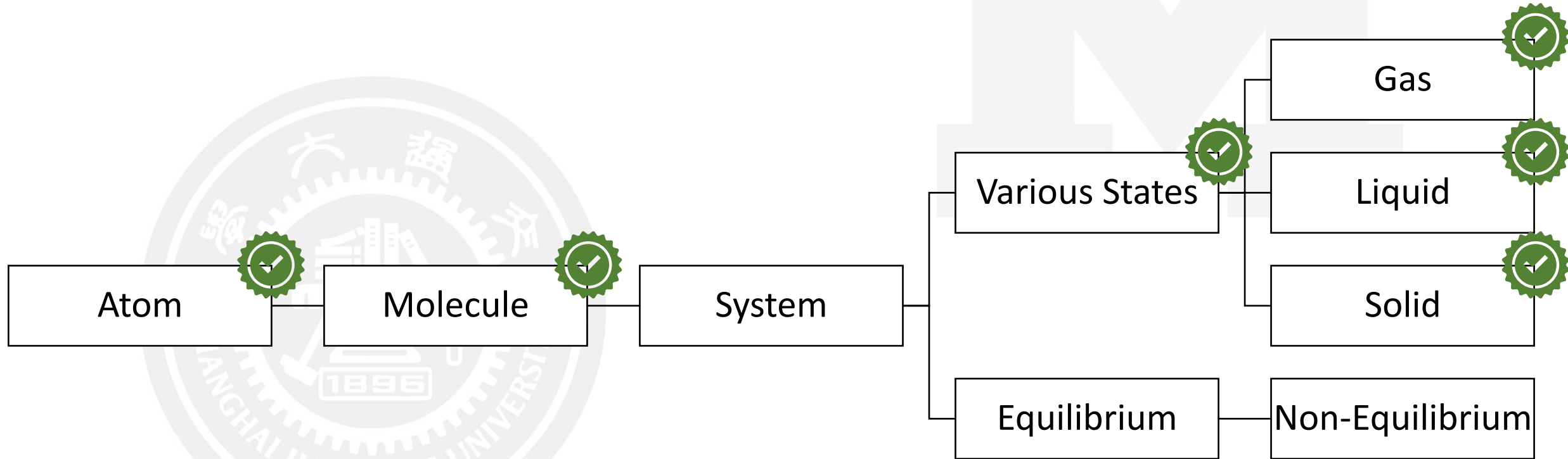
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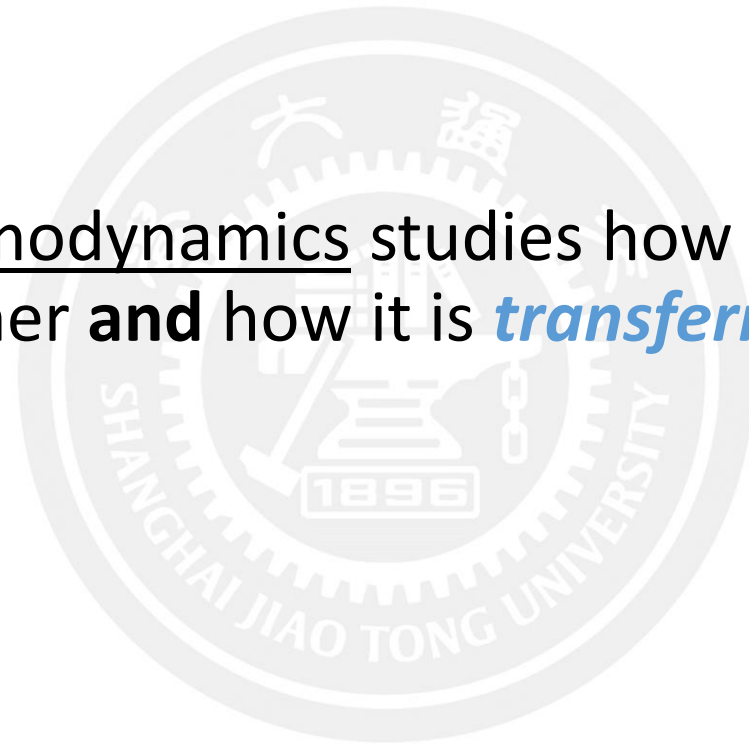
The Journey So Far



Heat (Q) and work (W) are forms of energy in the study of thermodynamics;

- First law studies energy as heat and work.
- Second law explains why it happens.
- Third law statistically calculates the second law.

Thermodynamics studies how energy is *transformed* from one *form* into another **and** how it is *transferred*.



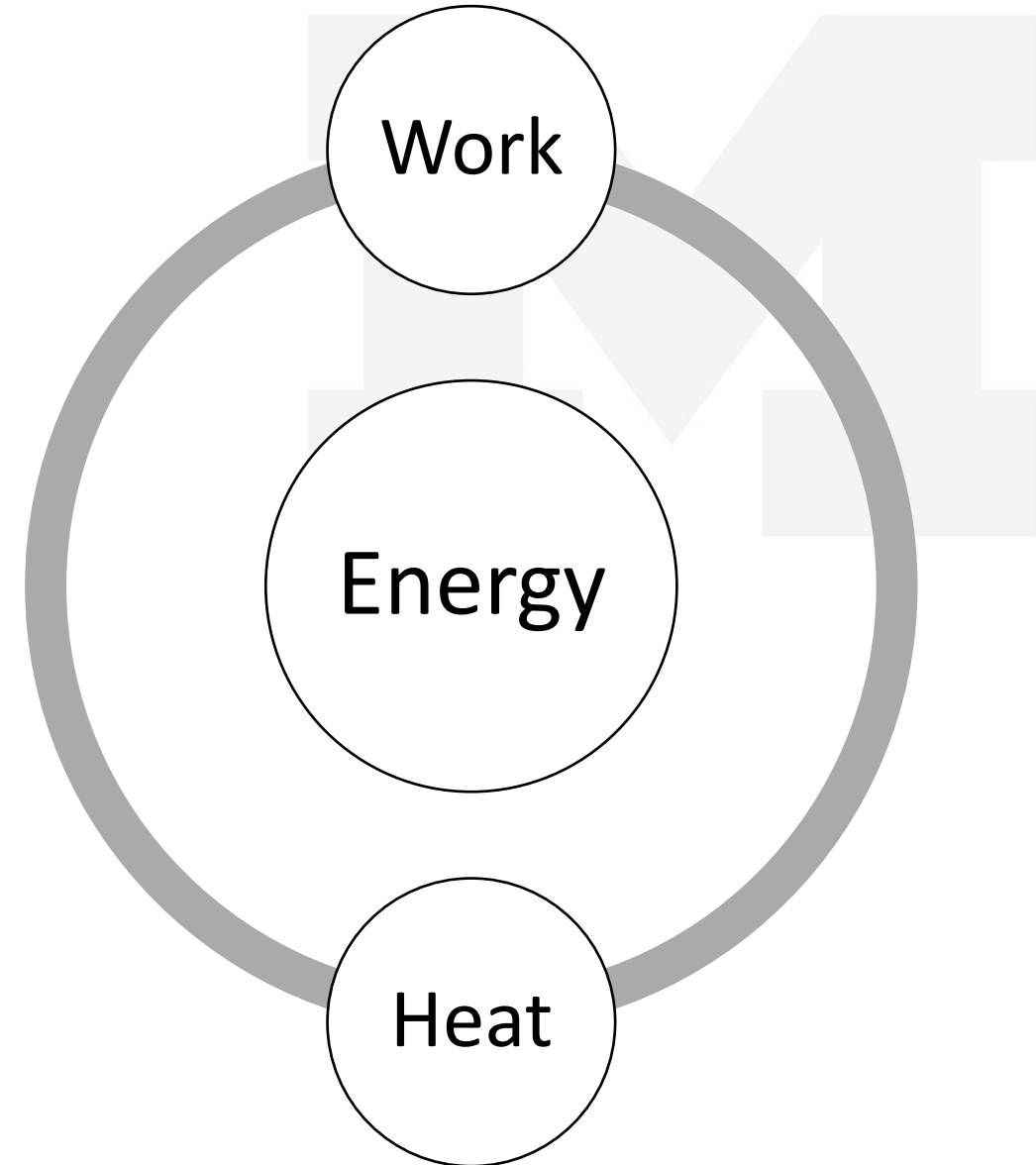
Thermodynamics is Central to Chemistry



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Thermodynamics:

Work and *Heat* are
Energy

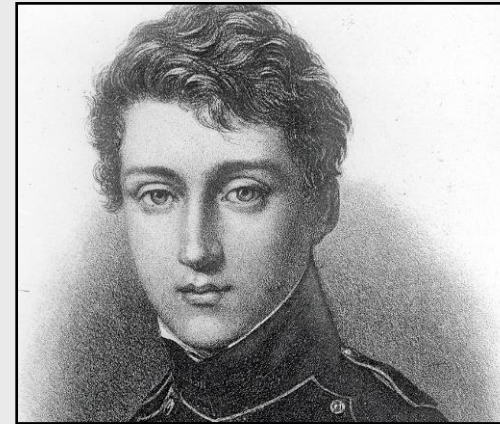


Historical Views on Heat

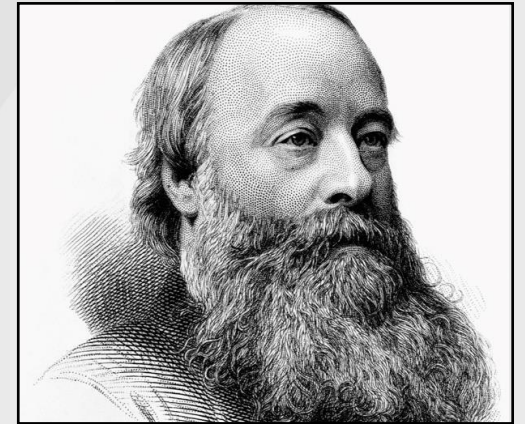
Heat was thought of as a fluid, flowing from a hot to a cold substance.

Sadi Carnot, a French engineer, believed *heat flowed to produce work*, just as water flowed to turn a water wheel.

James Joule, an English physicist, showed that *energy* can be *transformed* into *heat* and/or *work*.



Sadi Carnot



James Joule

System versus Surroundings

The **system** and the **surroundings** jointly make up the **universe**.

You can “**Open**” the System to the surroundings (p , V , T all change).

You can “**Close**” the System to the surroundings (put a lid on it—constant V (isochor)).

You can “**Isolate**” the System by preventing temperature from escaping (constant T (isothermal)).

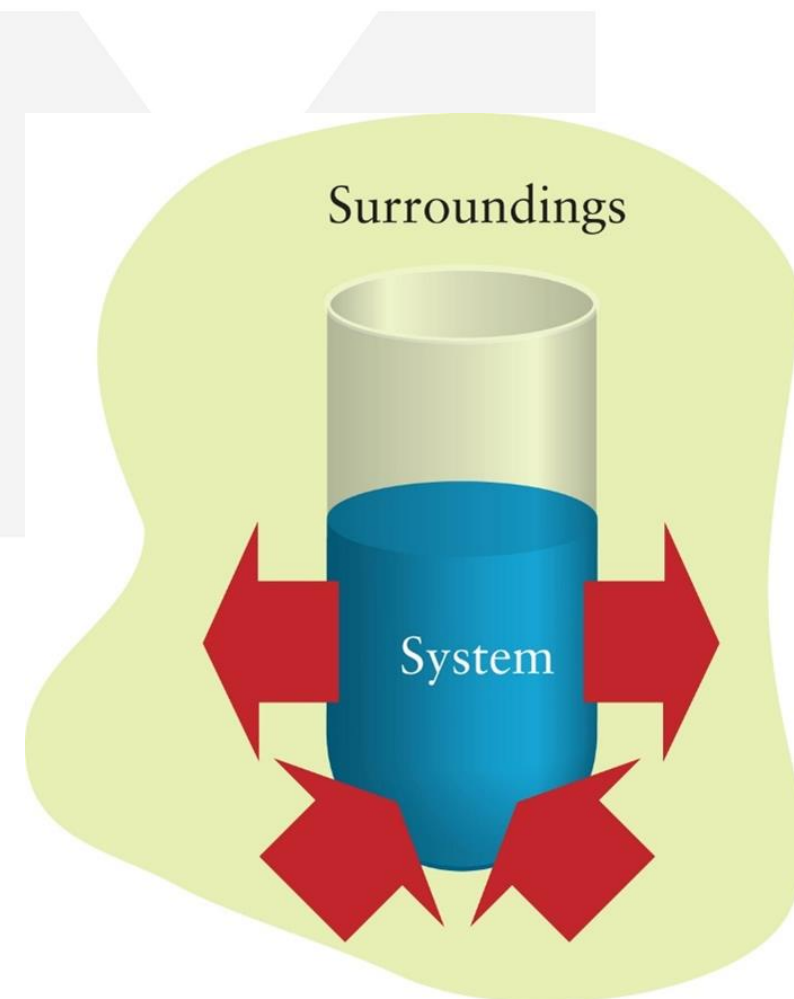


Figure 4A.3
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Universe = System + Surroundings

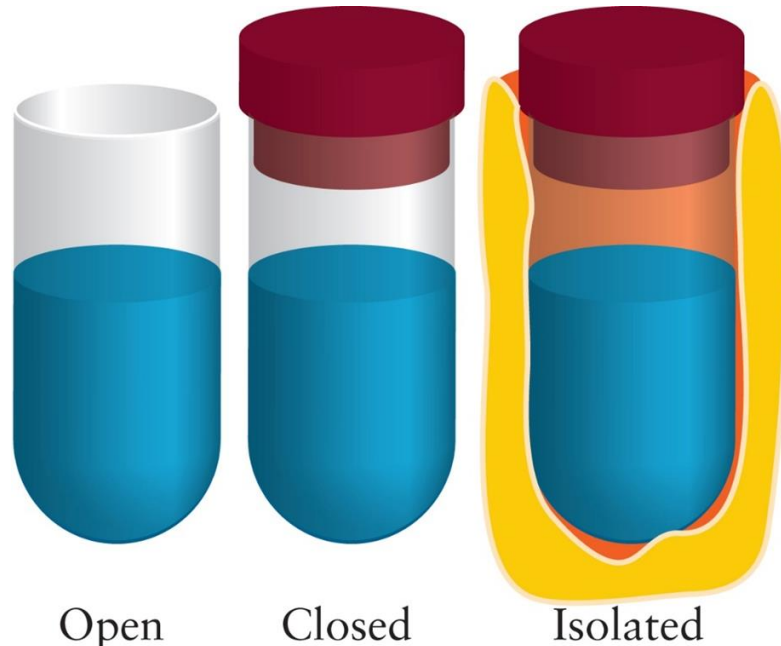


Figure 4A.4
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An **open system** can exchange both matter and energy with the surroundings.

A **closed system** has a fixed amount of matter, but it can **exchange energy** with the surroundings, e.g., a cold pack used to treat athletic injuries.

Isolated systems have no contact with their surroundings, e.g., a sealed, insulated, rigid container like a thermos flask.

Internal Energy U



In thermodynamics, the capacity of a **system** to do work is called its internal energy U .

Absolute internal energy is **not measurable** because it includes the energies of all the atoms, their electrons, and the components of their nuclei.

The best we can do is to measure **changes** in internal energy, or ΔU :

$$\Delta U = U_{final} - U_{initial}$$

$$\Delta U = Q + W$$

Internal Energy U



If a system **does** 15 J of work (as when your body moves), it **uses up** some of its store of energy, so we say its internal energy has fallen by 15 J and write $\Delta U = -15 \text{ J}$.

A negative value of $\Delta U = -15 \text{ J}$ means U has decreased.

If we **do work ON** the system, let's say 15 J of work, we say its internal energy has increased by 15 J and write $\Delta U = +15 \text{ J}$ (winding a spring or eating a sandwich increases U of the system).

A positive value of $\Delta U = +15 \text{ J}$ means U has increased.



Work



The most fundamental property in thermodynamics is work, or motion against an opposing force.

Work = **opposing force** × **distance moved**

The SI unit for work (energy) is the Joule [J] where

$$1 \text{ J} = 1 \text{ N} \cdot \text{m} = 1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

Work is done when:

- Raising a weight against the pull of gravity
- A chemical reaction in a battery, when it pushes an electric current through a circuit
- A gas in a cylinder when it expands and pushes back a piston

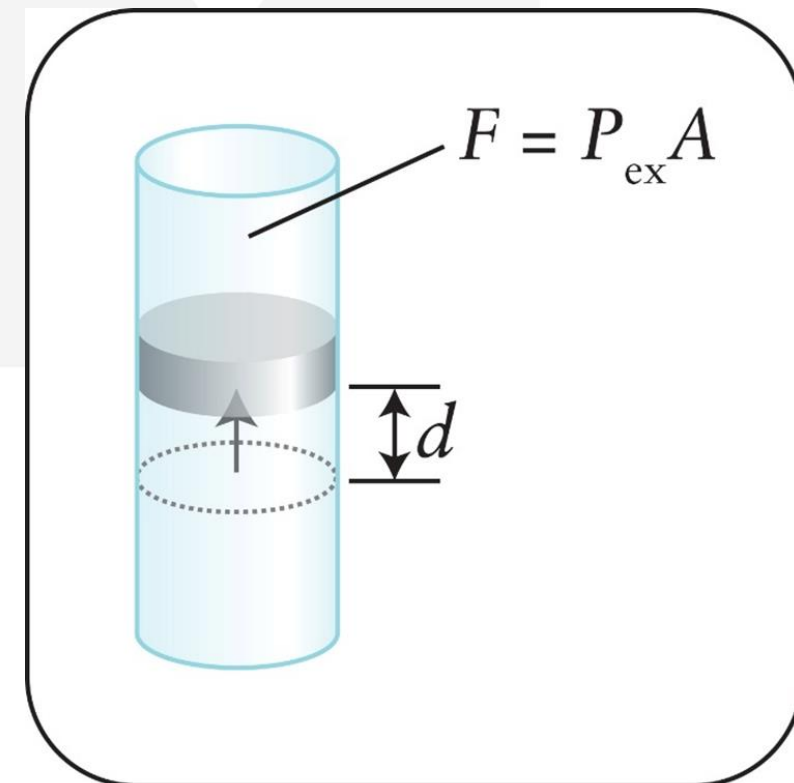


Expansion work is a **change in volume of a system**.

- Expansion work occurs when a gas expands in a cylinder, pushing back a piston which pushes out against the atmosphere.

Non-expansion work can be the flow of electrical current.

- Chemical reactions do non-expansion work by causing electrical current to flow.



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Work due to volume change

$$W = -p_{ex} \cdot \Delta V$$

and denoted “ $-$ ” because it is assumed that work will be done, and the internal energy will therefore decrease.

Two forms of Expansion Work ($W = p\Delta V$):

1. Expansion at constant pressure (isobar)
2. Expansion at constant temperature with changing pressure (isothermal)

$$V = \frac{nRT}{p}$$

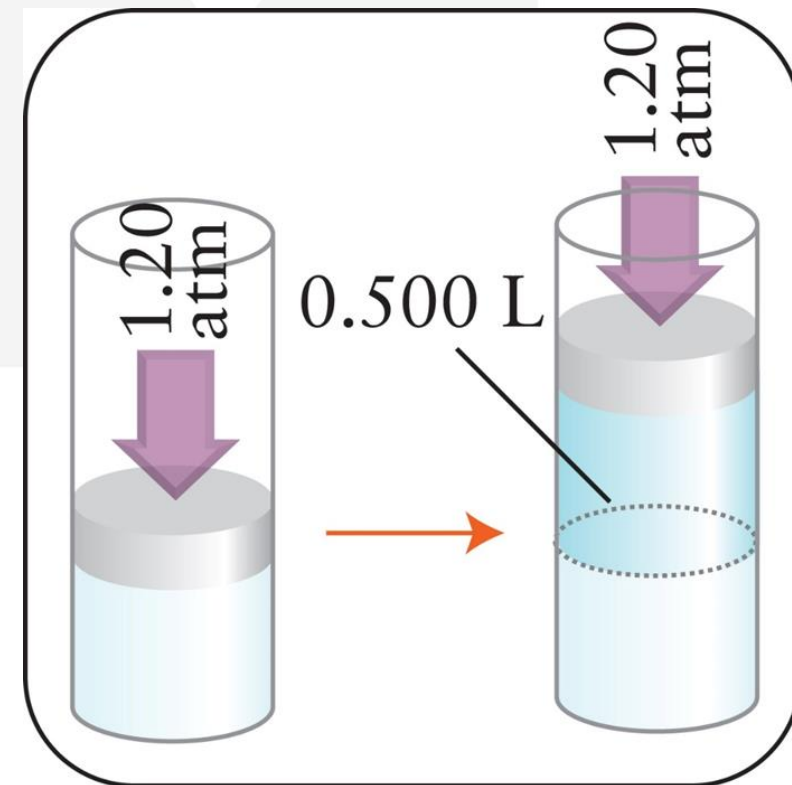
Expansion Work

Work = opposing force \times distance moved

The **opposing force** is the external pressure pushing against the outer face of the piston.

How much expansion work is done is seen when the system expands, ΔV , against the external pressure p_{ex} .

Work is done when the gas expands, and the piston pushes against the opposing force (atmospheric pressure).



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Pressure-Work Relationship: Expansion

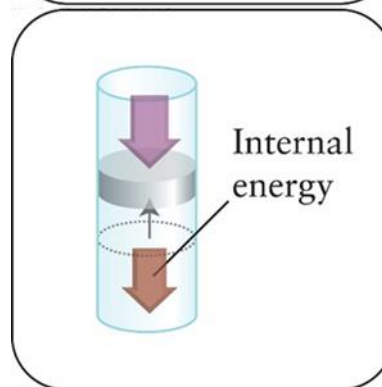
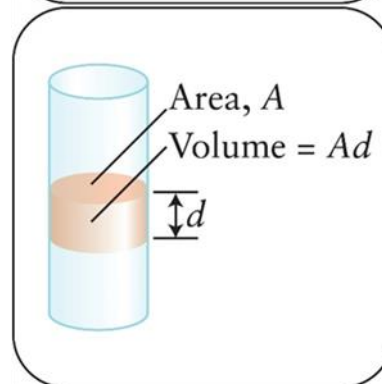
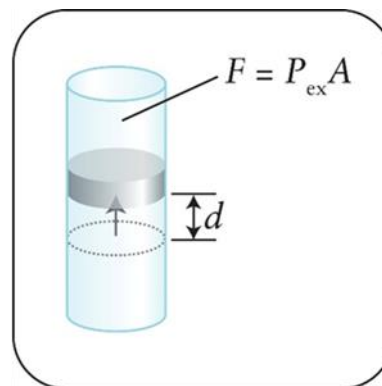


$$W = -p_{ex} \cdot (A \cdot d)$$

$$(A \cdot d) = \Delta V$$

$$W = -p_{ex} \cdot \Delta V$$

ΔU is negative for an expansion.



The system does expansion work by **pushing** against the opposing pressure $\left(\frac{F}{A}\right)$, so the system loses energy as work and ΔU is negative.

- If ΔV is positive (an expansion), W is negative.
- If ΔV is negative (contraction), W is positive.

Free Expansion



If the external pressure is zero (a vacuum), then $W = 0$

No expansion work is done in a vacuum because there is no opposing force – there is nothing to push against.

Expansion against **zero pressure** is called **free expansion**.

Changing External Pressure



Work is a measure of changes in p and V .

Measuring work where V changes in either direction *as a* "reversible" expansion must be done in "infinitesimal" changes.

Of course, this means that pressure increases or decreases infinitesimally as well.

These reversible processes are of the greatest importance in thermodynamics, and we shall encounter them many times.

In thermodynamics, a **reversible process** is a process which can be **turned back**, so that both the system and the surroundings **return to their original states**, with no other change anywhere else in the universe.

An ideal thermodynamically reversible process is **free of dissipative losses** and therefore the magnitude of work performed by or on the system is maximized.

We will learn more about this maximized work later.

Measuring: Isothermal Work with Changing p_{ex}

The simplest **reversible** change is an **isothermal** (constant temperature) expansion of an ideal gas.

The criterion for isothermal expansion is that the temperature remains unchanged.

$$V = \frac{nRT}{p}$$

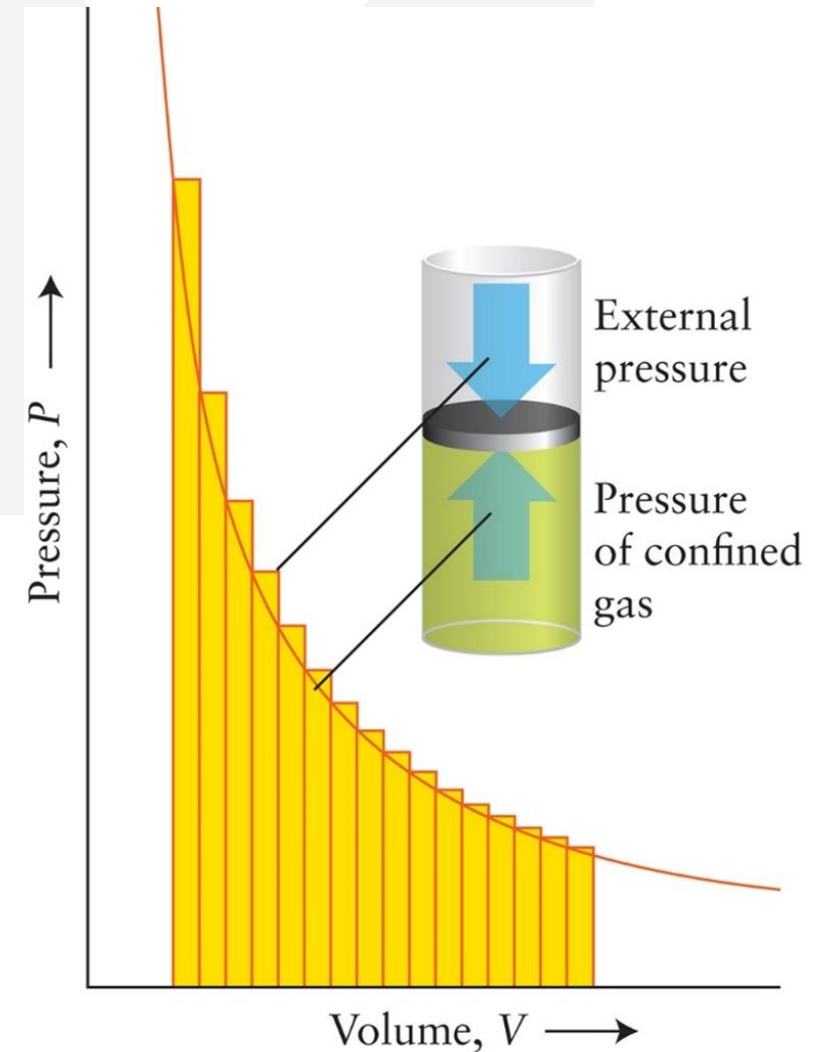


Figure 4A.6

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Calculating: Isothermal Work with Changing p_{ex}

The symbol for infinitesimal change in calculus is d , so small changes in volume are dV .

An infinitesimal change volume causes an infinitesimal change in work according to:

$$dW = -p_{ex}dV$$

Matching external to the internal pressure ($p_{ex} = p$):

$$dW = -pdV$$

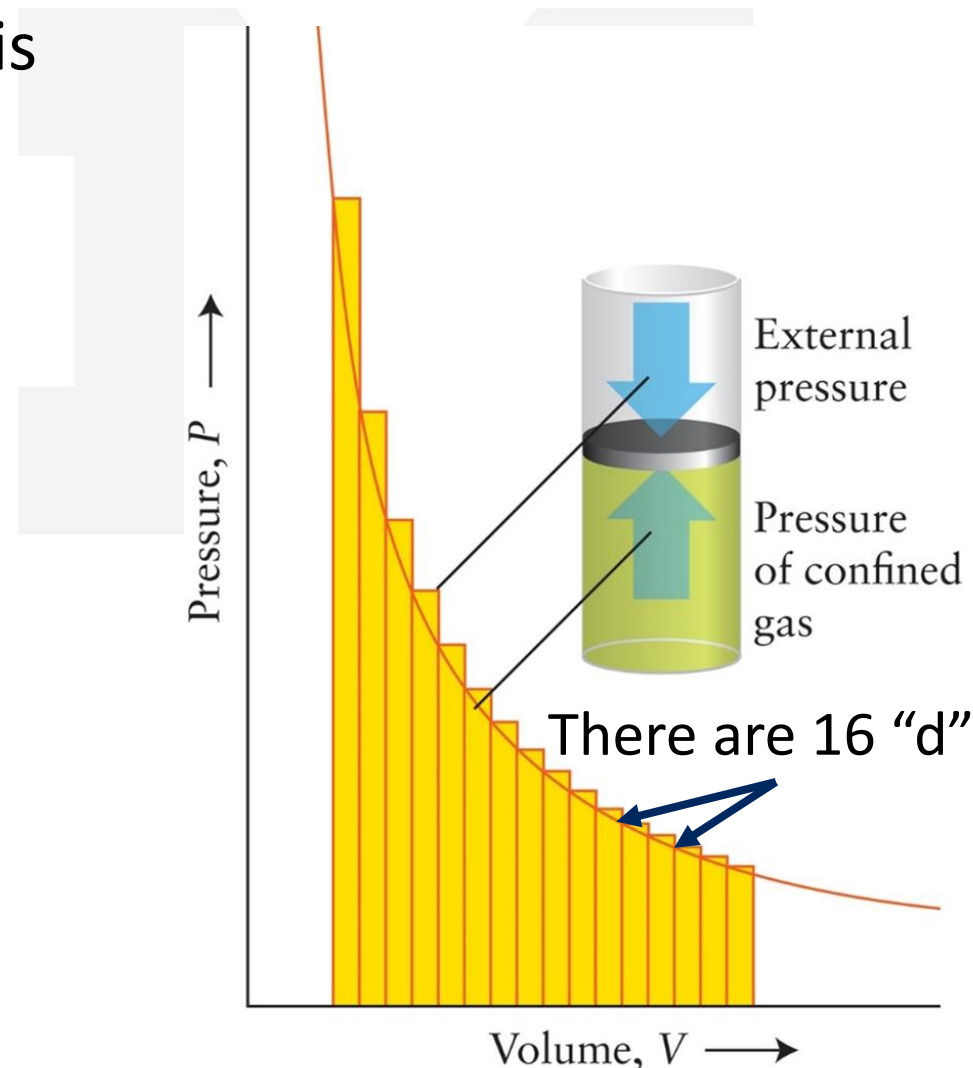


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Calculating: Isothermal Work with Changing p_{ex}



$$dW = -pdV$$

Since $pV = nRT$ we can substitute $p = \frac{nRT}{V}$ for an ideal gas.

$$dW = -\frac{nRT}{V} dV$$

dW is the work for only **one change** in pV .

To find the work for ALL 16 bar's worth, we need the “total” work, so we must sum these up.

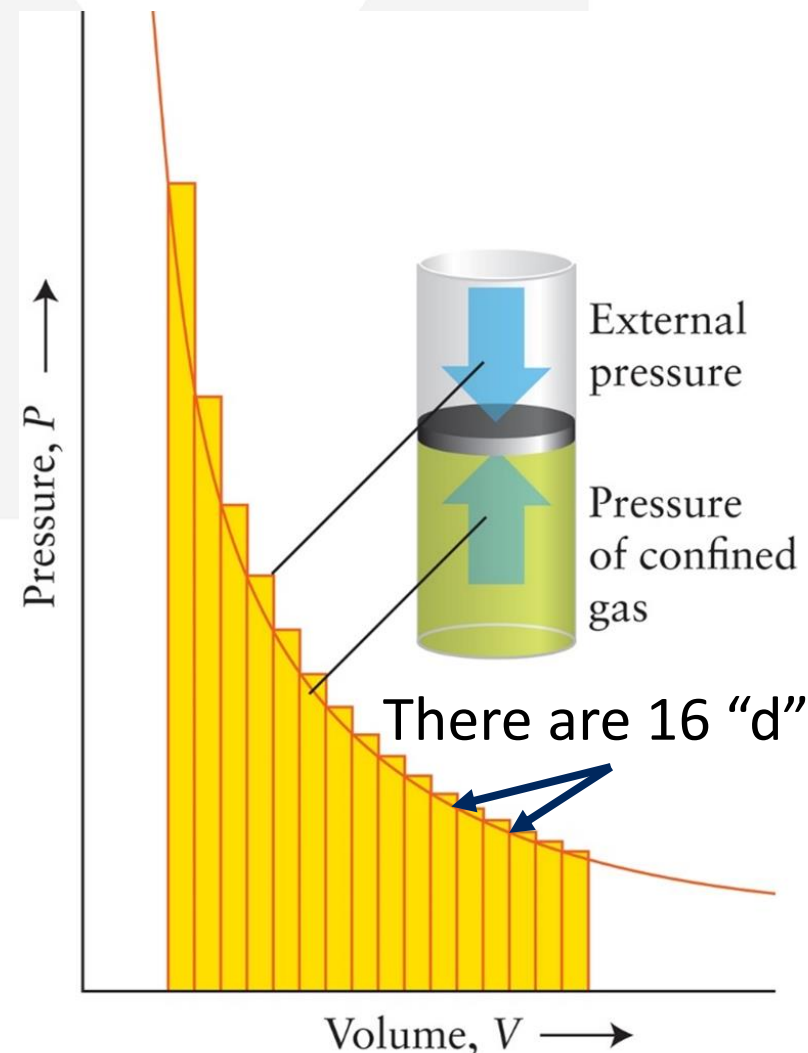


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Calculating: Isothermal Work with Changing p_{ex}



The total work is the sum (integral) of these infinitesimal contributions (as the volume changes).

The calculus integral symbol is \int , which we apply to both sides of

$$dW = -\frac{nRT}{V} dV$$

to get

$$\int dW = \int -\frac{nRT}{V} dV$$

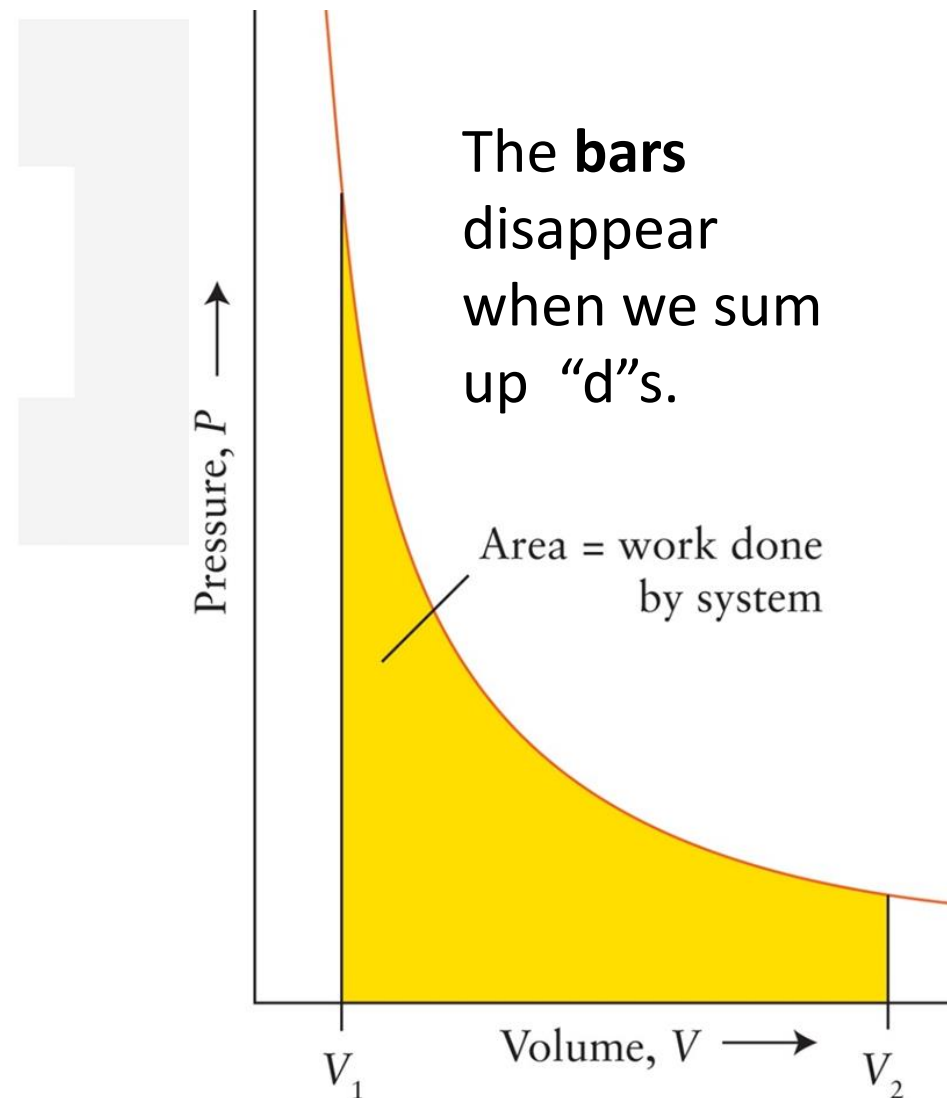


Figure 4A.7

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Calculating: Isothermal Work with Changing p_{ex}



$$\int dW = \int -\frac{nRT}{V} dV$$

Using calculus ($\int \frac{1}{x} dx = \ln x + \text{const.}$), we can solve for:

$$W = -nRT \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{dV}{V} = -nRT \cdot \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right)$$

isothermal work (constant temperature)

$$W_{\text{rev}} = -nRT \cdot \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right)$$

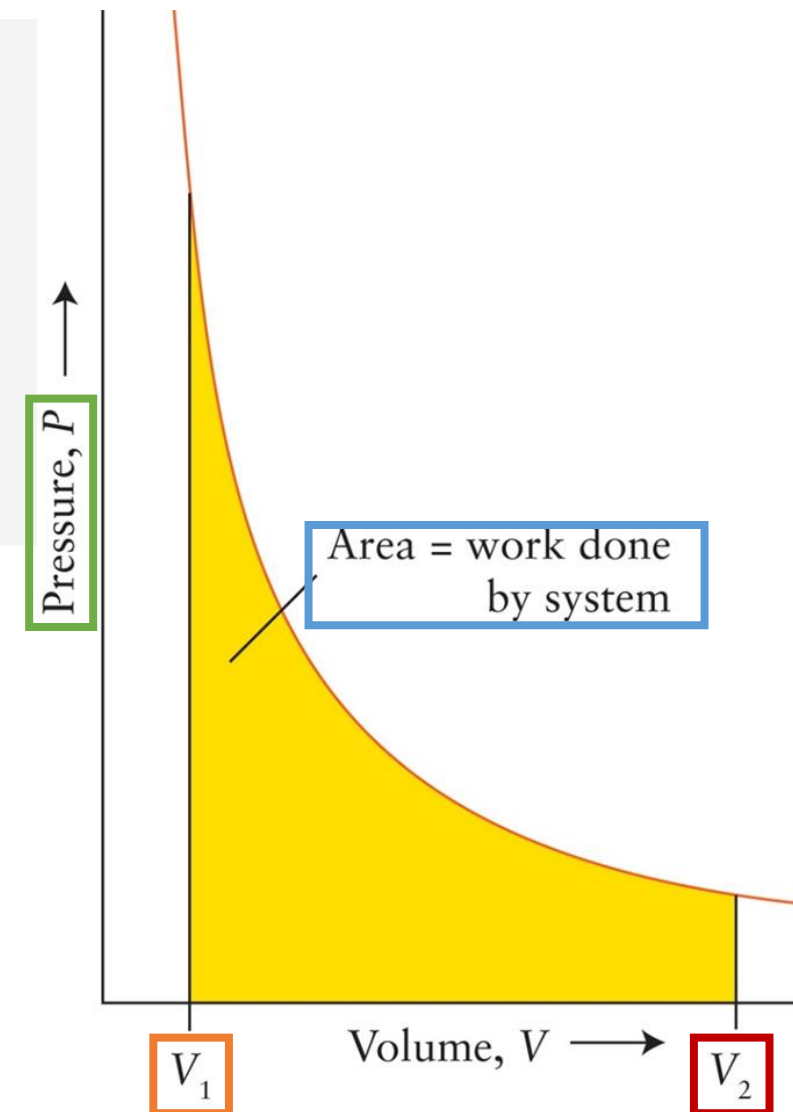


Figure 4A.7
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Summary: Work

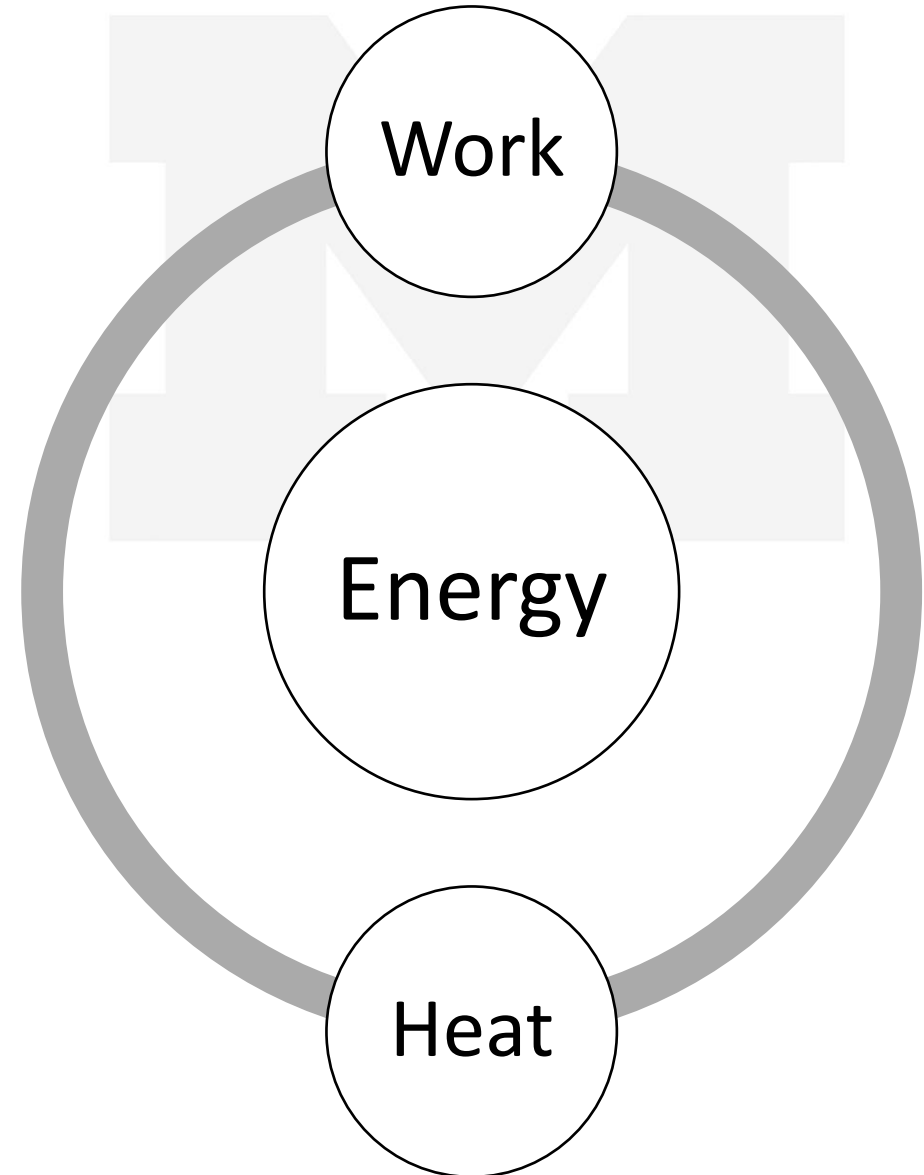
We know how to calculate the amount of work two ways:

1. For expansion against constant external pressure:

$$W = -p_{ex} \cdot \Delta V$$

2. For a reversible, isothermal expansion:

$$W_{rev} = -nRT \cdot \ln \left(\frac{V_{final}}{V_{initial}} \right)$$





Heat



$$\Delta U = Q + W$$

Is there a difference between heat and temperature?

Heat is not a substance, as originally thought by Sadi Carnot.

Heat is a **transfer** of energy: it is what physically happens when two objects at different temperatures touch.

Energetic molecules in higher-temperature regions vigorously stimulate slower-moving molecules in the lower-temperature region into higher energetic states.

Energy Transfer as Heat



$$\Delta U = Q + W$$

Heat is the transfer of energy as a result of a temperature difference. When energy is transferred as heat and no other processes occur, $\Delta U = Q$.

If **energy leaves** a *system* as heat, the internal energy of the system decreases and **-Q** is negative, then $Q = -10 \text{ J}$.

If **energy enters** a *system* as heat, the internal energy of the system increases and **+Q** is positive, then $Q = +10 \text{ J}$.

Heat capacity, C , measures heat transferred (Q), as energy to a system (or surroundings) to a corresponding change in temperature (ΔT):

$$C = \frac{Q}{\Delta T}$$

With the same amount of heat (Q), a larger heat capacity (C) produces only a small temperature change.

Heat Capacity



Specific heat:

$$C_s = \frac{C}{m}$$

m : mass

Molar heat capacity:

$$C_m = \frac{C}{n}$$

n : amount in moles

$$C_m = C_s \cdot M = \frac{C}{m} \cdot \frac{m}{n}$$

Also commonly used in the following forms:

specific heat capacity:

$$Q = m \cdot C_s \cdot \Delta T$$

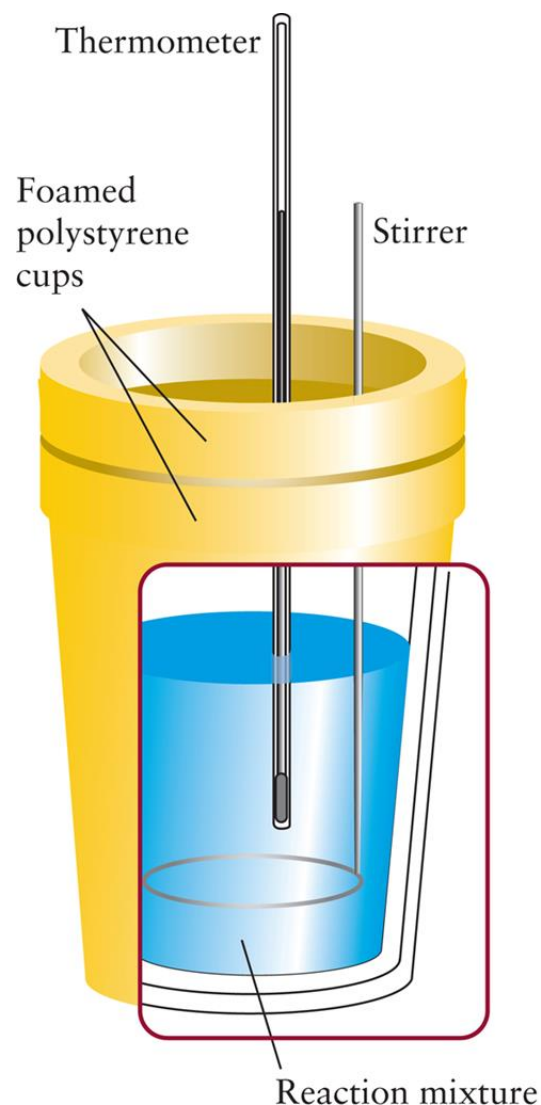
molar heat capacity:

$$Q = n \cdot C_m \cdot \Delta T$$

For Water the specific heat is

$4.18 \frac{\text{J}}{^\circ\text{C}\cdot\text{g}}$ or $4.18 \frac{\text{J}}{\text{K}\cdot\text{g}}$ and the molar

heat capacity is $75 \frac{\text{J}}{\text{mol}\cdot\text{K}}$.



A calorimeter is a common device to measure energy transferred as heat

1. A calorimeter has a **known** C_{cal} .
2. When a sample is placed in the calorimeter, **heat from the experiment goes into** the calorimeter.
3. ΔT of the calorimeter is the heat lost by the experiment **into** the calorimeter.
4. By knowing information about the calorimeter (1) and temperature changes (3), we can calculate the heat for our experiment:

$$Q = C_{cal} \cdot \Delta T$$

Figure 4A.11
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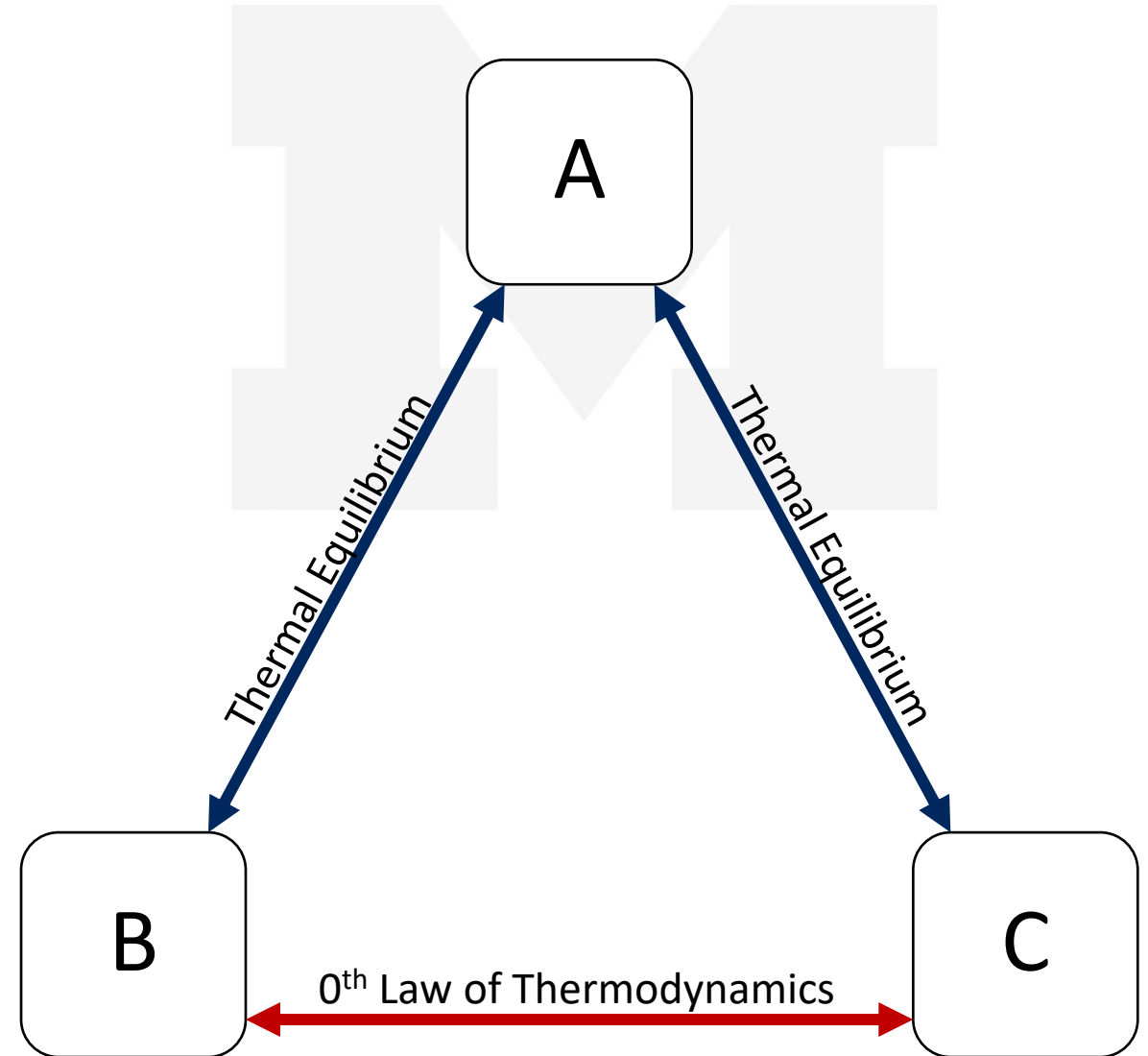
The First Law of Thermodynamics



The Zeroth Law of Thermodynamics



If two systems are **each**
in **thermal equilibrium**
with a **third system**,
then they are in
thermal equilibrium
with **each other**.



Perpetual Motion Machine?



$$\Delta U = Q + W$$

It is an experimental **fact**, supported by thousands of experiments, that we cannot take a system, make it do work, leave it isolated for a while, and then return to it to find its internal energy has returned to the original value and ready to provide the same amount of work again.

Every device that produces work must use fuel.

Patent offices have long since ceased accepting patents for “perpetual motion machines.”

The internal energy of an
isolated system is **constant**.

Internal energy is state function.

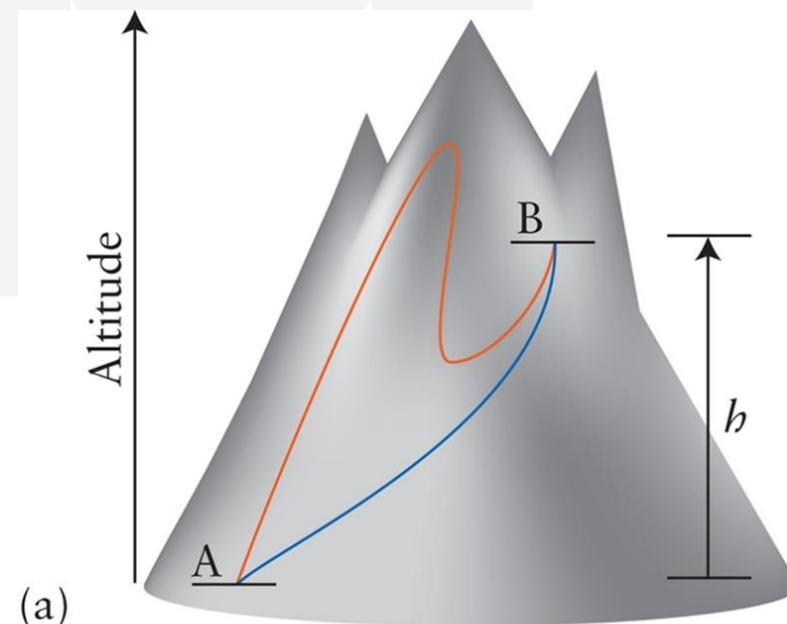
If we were to prepare a second system consisting of exactly the same amount of substance in exactly the same state as the first, and inspect that system, we would find that the second system has the same internal energy as the first system.

A property that **depends only on the current state** of the system and is **independent of how that state was prepared** is called a **state function**.

State Functions

A state function is like the altitude of a mountain. We may take any number of different paths between two huts on the mountain, but the change in *altitude* between the two huts is the same regardless of the path taken.

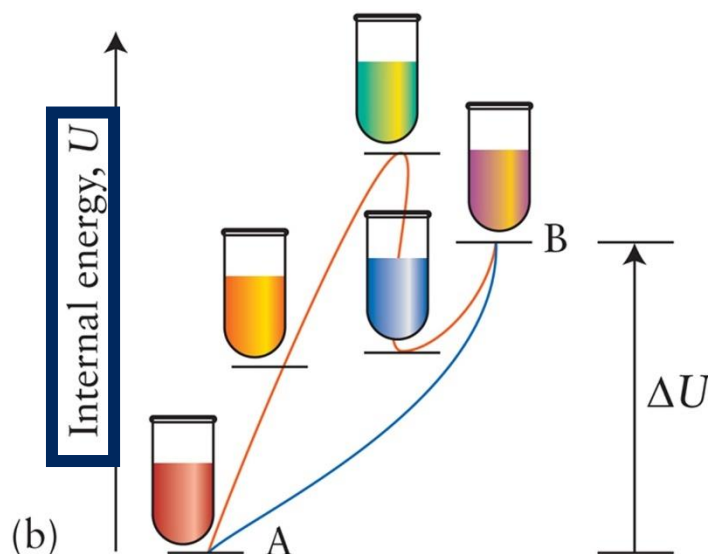
Pressure, volume, temperature, mass, and altitude of a system are also *state functions*, and so is internal energy.



(a)
Figure 4B.1a
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If in **one step** we raised a system's temperature, its internal energy would change by a certain amount.

In **multiple steps** of raising and lowering the temperature, we use a different amount of energy, but the change is the same.



(b)
Figure 4B.1b
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The net change (A to B) in the **internal energy** is exactly **the same**.

Example



In the next example, the internal energy, $\Delta U = Q + W$, is calculated by two different paths, both over the same range.

- a) One path calculates internal energy only reversibly.
- b) The other path is a combination of both reversible and irreversible.

The biggest difference between the two is that for a reversible process the temperature remains constant (isothermal).

Also, remember that all isothermal expansions are the most efficient (though not common).

Example



Suppose that 1.00 mol of ideal gas molecules at 292 K and at 3.00 atm expands from 8.00 L to 20.00 L and has a final pressure of 1.20 atm.

Determine for each path the work done, the heat transferred, and the change in internal energy (W , Q , and ΔU).

(Hint: ideal gas isothermal expansion $\Delta U=0$)

(a) Path A is an isothermal, reversible expansion.

(b) Path B has two parts. In step 1, the gas is cooled at constant volume until its pressure has fallen to 1.20 atm. In step 2, it is heated and allowed to expand against a constant pressure of 1.20 atm until its volume is 20.00 L and $T = 292$ K.

Example: Path A

(a) Path A is an isothermal, reversible expansion.

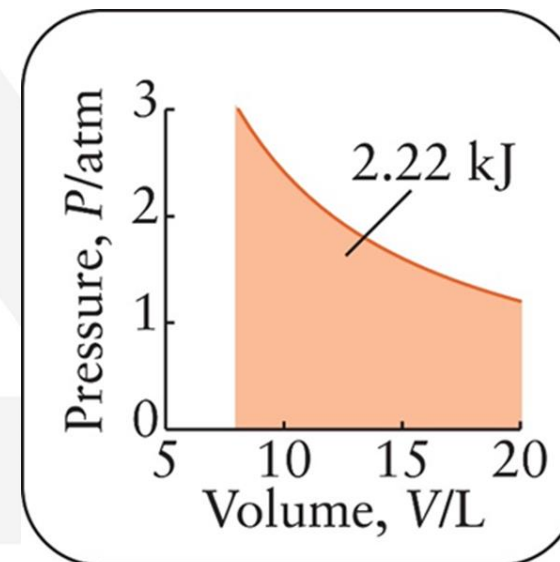
Isothermal, reversible work:

$$W_{rev} = -nRT \cdot \ln \left(\frac{V_{final}}{V_{initial}} \right)$$

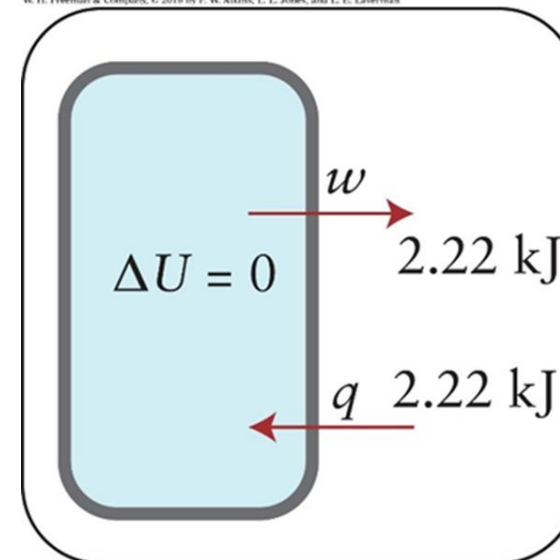
$$W_{rev} = -1.00 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 292 \text{ K} \cdot \ln \left(\frac{20.00 \text{ L}}{8.00 \text{ L}} \right) = -2.22 \text{ kJ}$$

From $\Delta U = Q + W = 0$:

$$Q = -W = +2.22 \text{ kJ}$$

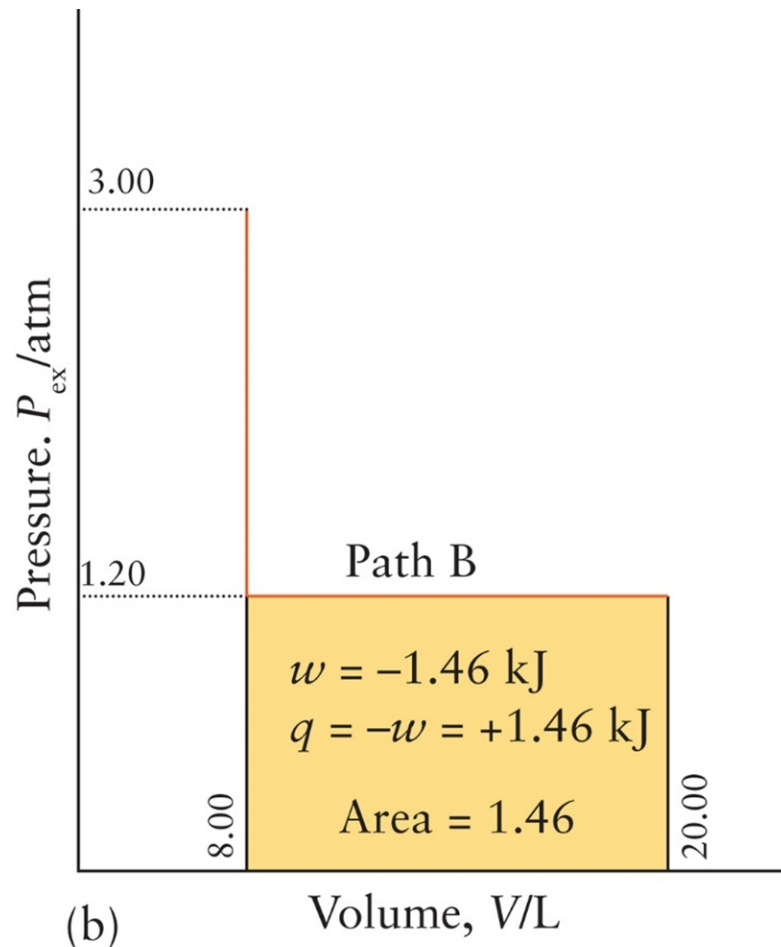


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Example: Path B



(b) Path B has two parts. In step 1, the gas is cooled at constant volume until its pressure has fallen to 1.20 atm. In step 2, it is heated and allowed to expand against a constant pressure of 1.20 atm until its volume is 20.00 L and $T = 292 \text{ K}$.

Step 1: cooling at constant V ($p \downarrow$ $T \downarrow$)

no work or $W = 0$

Example: Path B

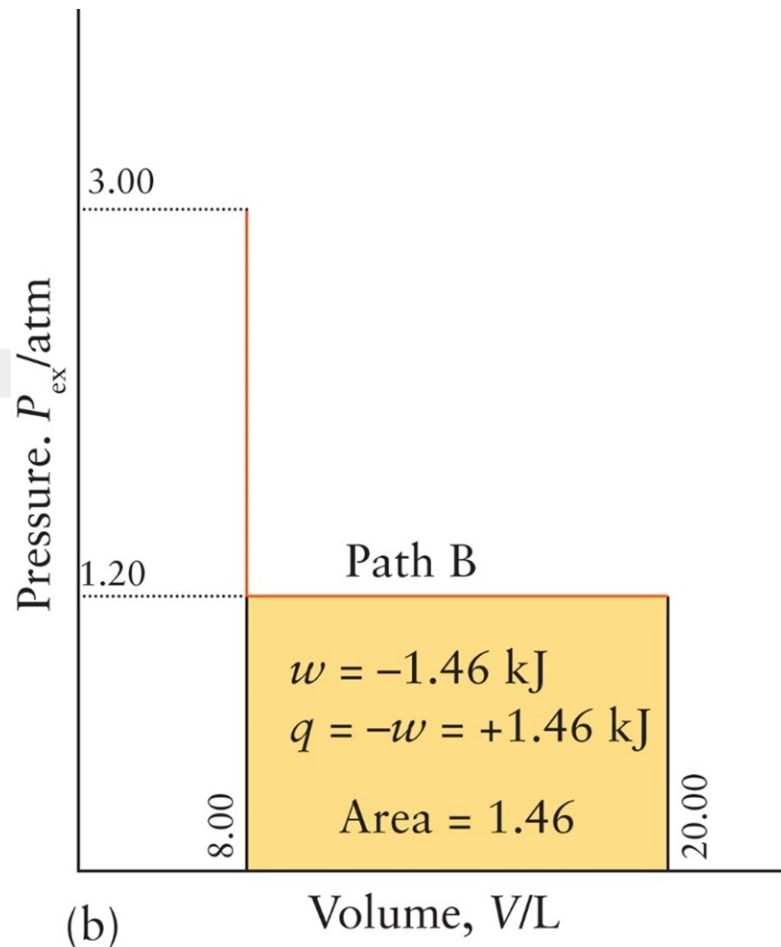


Figure 4B.3b
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Step 2: expansion at constant p ($V \uparrow$ $T \uparrow$)

$$W = -p_{\text{ex}} \cdot \Delta V = -p_{\text{ex}} \cdot (V_{\text{final}} - V_{\text{initial}})$$

$$W = 1.20 \text{ atm} \times \frac{101.325 \text{ J}}{\text{L} \cdot \text{atm}} \times (20.00 \text{ L} - 8.00 \text{ L}) = -1.46 \text{ kJ}$$

Combining Step 1 and Step 2:

$$\text{Step 1} + \text{Step 2} = 0 + (-1.46 \text{ kJ}) = -1.46 \text{ kJ}$$

From $\Delta U = Q + W = 0$:

$$Q = -W = +1.46 \text{ kJ}$$

Example

Path A: since $\Delta U = 0$, heat flows to maintain constant temperature and constant internal energy.

Path B: overall, the outflow of heat in the cooling step combined with the work done corresponding to the area under the curve is less than Path A.

$$\Delta U = 0 \text{ for both}$$

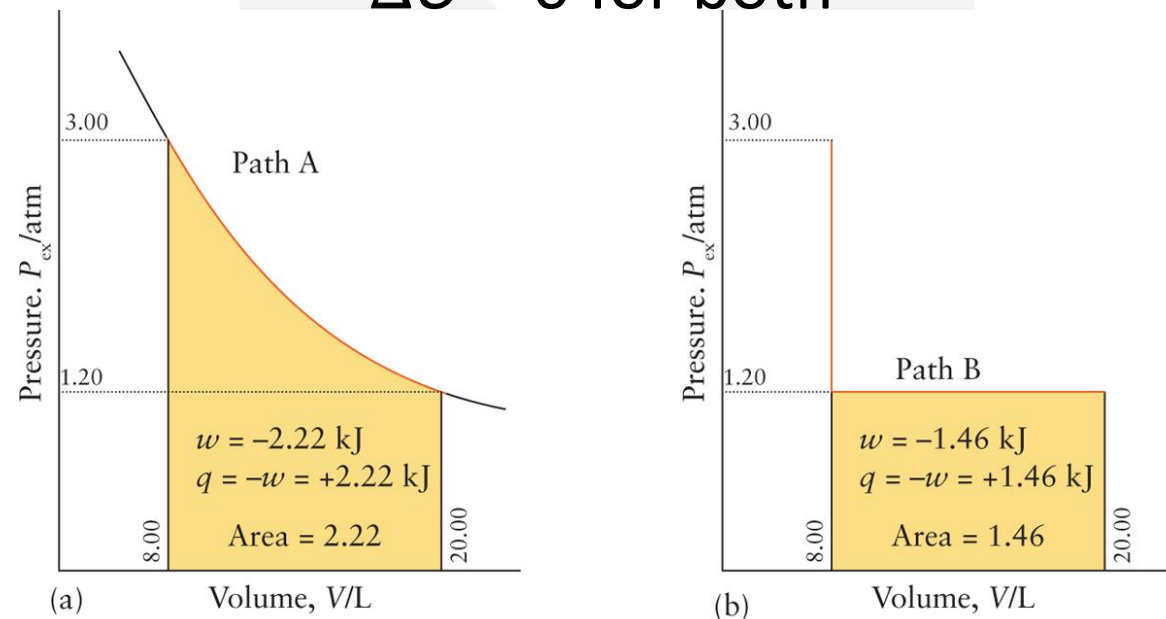


Figure 4B.3

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Isothermal, reversible does **more work**, +2.22 kJ.

Nonreversible does **less work**, +1.46 kJ.

Interlude: The Origin of Internal Energy



Internal energy, U , is energy stored in a system as kinetic energy and potential energy.

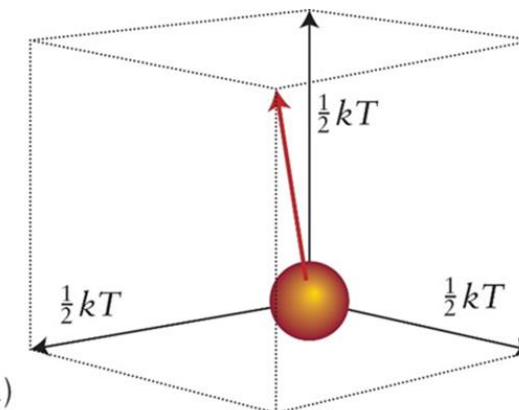
Heating a gas always makes the molecules move faster, so they will have a higher E_{kin} .

Interlude: The Origin of Internal Energy



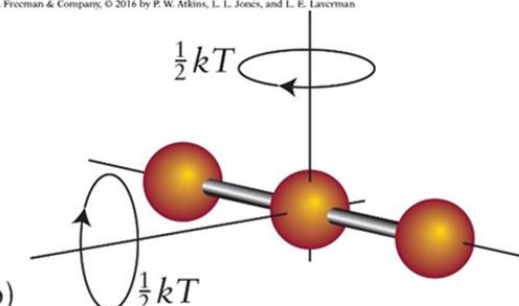
Molecules (not atoms) have several types of kinetic energy:

- Translation E_{kin} , moving through 3 dimensions
- Rotational E_{kin} , 2 rotating motions for **linear** molecules
- Rotational E_{kin} , 3 rotating motions for **nonlinear** molecules
- [Vibrational E_{kin} : most molecules at room temperature do not vibrate substantially so this is ignored here.]



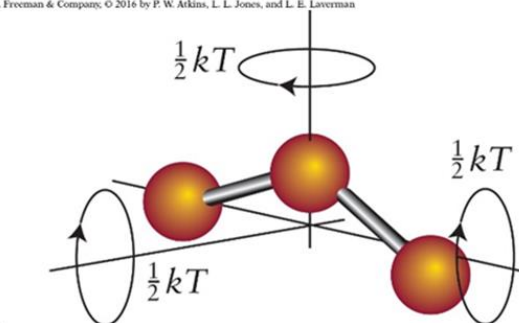
(a)

Figure 4B.5a
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(b)

Figure 4B.5b
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(c)

Figure 4B.5c
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Interlude: The Origin of Internal Energy



Translational kinetic energy is expressed as $\frac{1}{2}mv^2$.

The equipartition theorem (not derived here) states the average value of **each contribution** at a temperature T is **equal** to $\frac{1}{2}k_B T$, so for translational E_{kin} :

$$3 \times \frac{1}{2}k_B T = \frac{3}{2}k_B T$$

All directions contribute the same amount of energy.

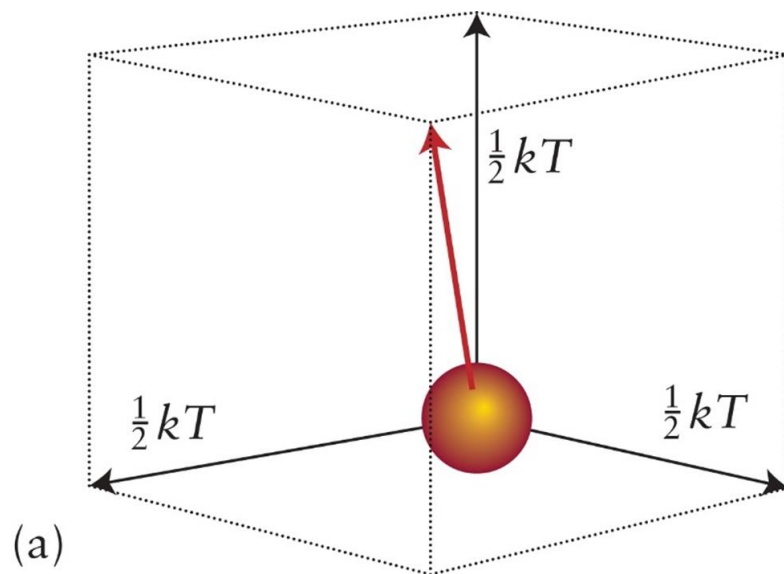


Figure 4B.5a
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“Equipartition” means energy is shared (partitioned) equally over all modes (translational, rotational, and vibrational).

Interlude: The Origin of Internal Energy



The **equipartition theorem** states that **translational E_{kin}** is

$$E_{kin} = 3 \times \frac{1}{2} k_B T = \frac{3}{2} k_B T$$

$$k_B = \frac{R}{N_A} = 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

Boltzmann's constant

It follows that for molar internal energy:

$$\mathbf{U} = \frac{3}{2} \mathbf{N_A k_B T} = \frac{3}{2} \mathbf{RT}$$

As $RT = 2.48 \frac{\text{kJ}}{\text{mol}}$ at 25 °C:

$$E_{kin} = \frac{3}{2} RT = 3.72 \frac{\text{kJ}}{\text{mol}}$$

Interlude: The Origin of Internal Energy



For linear molecules (b):

$$\text{Translational } E_{kin}: \quad \frac{3}{2}RT = 3.72 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Rotational } E_{kin}: \quad \frac{2}{2}RT = 2.48 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Total } E_{kin}: \quad \frac{5}{2}RT = 6.02 \frac{\text{kJ}}{\text{mol}}$$

For nonlinear molecules (c):

$$\text{Translational } E_{kin}: \quad \frac{3}{2}RT = 3.72 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Rotational } E_{kin}: \quad \frac{3}{2}RT = 3.72 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Total } E_{kin}: \quad \frac{6}{2}RT = 7.44 \frac{\text{kJ}}{\text{mol}}$$

Conclusion: **Internal energy** is stored as molecular kinetic and potential energy; It is estimated at $7.44 \text{ kJ} \cdot \text{mol}^{-1}$ at room temperature for nonlinear molecules and $6.02 \text{ kJ} \cdot \text{mol}^{-1}$ for linear molecules.

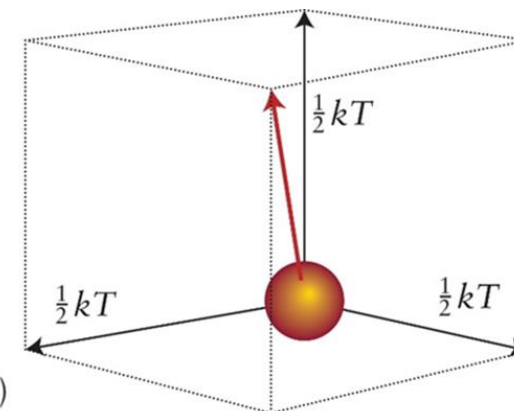


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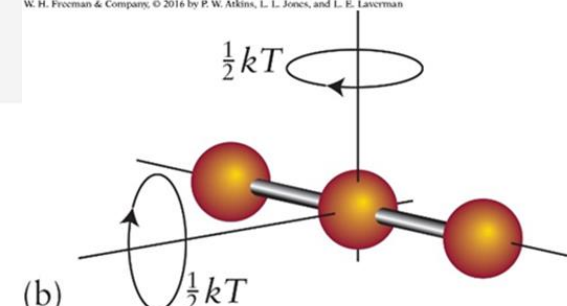


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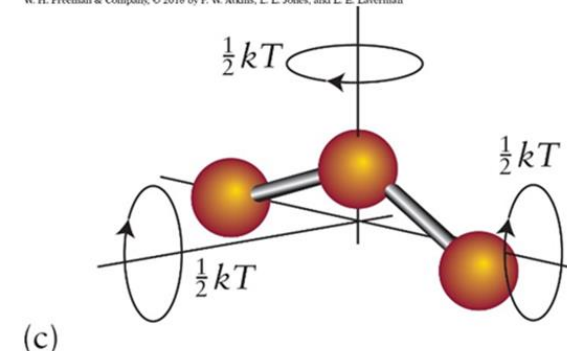


Figure 4B.5c
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Internal energy, U , is both heat and work:

$$\Delta U = Q + W$$

Our attention now shifts to the chemistry laboratory.

Constant Volume Scenario



$$\Delta U = Q + W$$

And for non-expansion work $W = 0$.

So, at constant volume:

$$\Delta U = Q$$

In this case **energy supplied** is strictly **heat**, Q only.

Constant Pressure Szenario



Gases are free to expand (or contract), **but** they are working against the atmosphere, which is acting as the opposing force in a piston.

So, for chemists we must use another state function to keep track of our energy at ***constant pressure***.

The new state function is called **enthalpy, H** :

$$H = U + pV$$

U , p , and V are the internal energy, pressure, and volume of the *system*.

Enthalpy is a **state function** because U (from the first law), p , and V are also state functions.

Constant pressure means the system is open, and the work is pushing against the atmosphere; that is, the constant pressure is the constant pressure of the atmosphere.

It follows from enthalpy, $H = U + pV$, that changes at constant pressure are expressed as:

$$\Delta H = \Delta U + p \cdot \Delta V$$

Substituting $\Delta U = Q + W$:

$$\Delta H = Q + W + p \cdot \Delta V$$

For a system doing expansion work only, we can substitute $W = -p_{ex} \cdot \Delta V$, yielding:

$$\Delta H = Q + (-p_{ex} \cdot \Delta V) + p \cdot \Delta V$$

Heat Transfer at Constant Pressure



$$\Delta H = Q + (-p_{ex} \cdot \Delta V) + p \cdot \Delta V$$

Now, *if we leave our system open to the atmosphere*, the pressure of the system is the same as the external pressure, so $p = p_{ex}$:

$$\Delta H = Q + (-p_{ex} \cdot \Delta V) + p_{ex} \cdot \Delta V$$

The last two terms cancel each other out, to give us:

$$\Delta H = Q$$

(at constant pressure)

Previously:

$$\Delta U = Q$$

(at constant volume)

Enthalpy: $\Delta H = Q$



For a chemical reaction **open to the atmosphere**, or at constant pressure, the **heat released** or **required** is the **enthalpy of the system**.

We note that

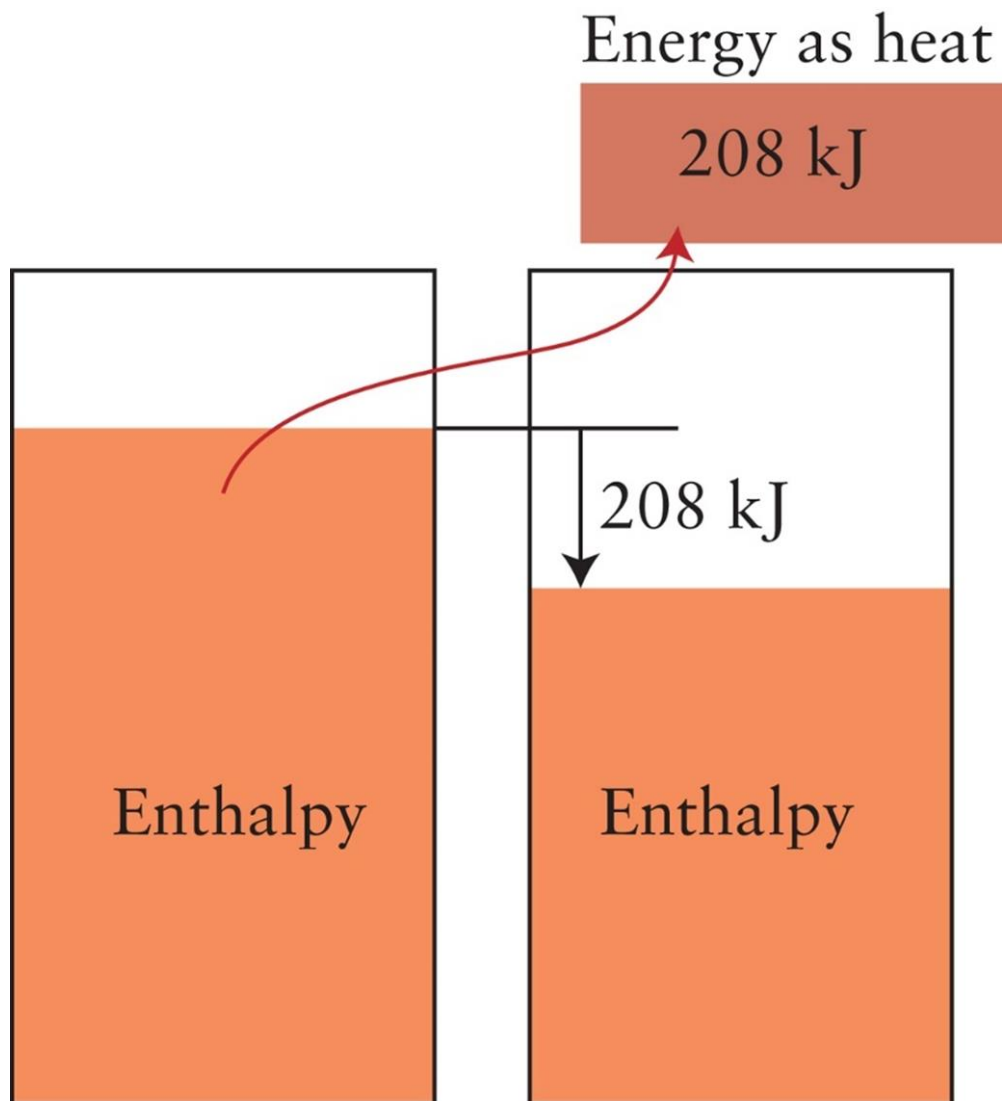
$\Delta H < 0$ for **exothermic** reactions, “-”,

whereas

$\Delta H > 0$ for **endothermic** reactions, “+”.

Note: We have ΔH , and this follows the first law even though there is no work term. Remember that ΔH is in a constant pressure (open to the atmosphere) scenario.

Enthalpy: $\Delta H = Q$



Exothermic reactions

The enthalpy of a system is like a measure of the height of water in a reservoir.

When a reaction releases 208 kJ of heat at constant pressure, the "reservoir" falls by 208 kJ and

$$\Delta H = -208 \text{ kJ}.$$

Figure 4C.1

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Enthalpy: $\Delta H = Q$

Endothermic reactions

If an endothermic reaction absorbs 100 kJ of heat at constant pressure, the height of the enthalpy “reservoir” rises by 100 kJ and

$$\Delta H = +100 \text{ kJ}.$$

Energy as heat

100 kJ

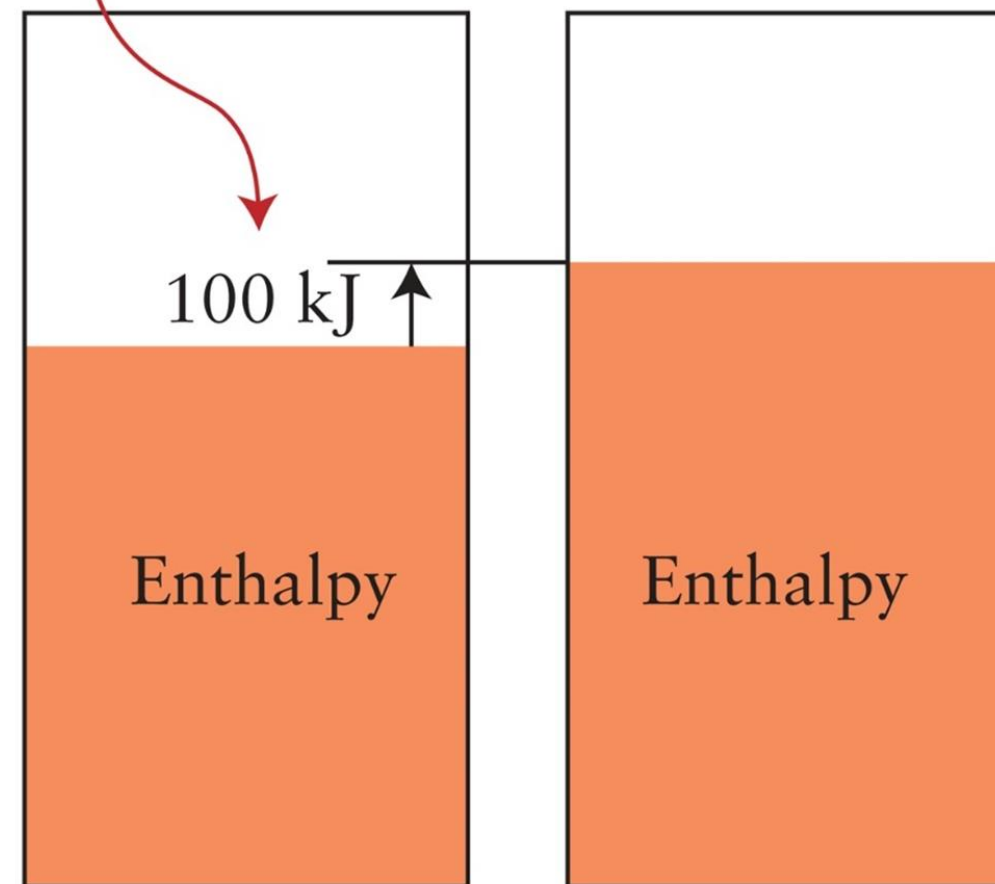


Figure 4C.2

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Heat Capacity at Constant V and Constant p



The definition of heat capacity:

$$C = \frac{Q}{\Delta T}$$

At **constant volume**:

$$\Delta U = Q$$

Therefore:

$$C_V = \frac{\Delta U}{\Delta T}$$

At **constant pressure**:

$$\Delta H = Q$$

Therefore:

$$C_p = \frac{\Delta H}{\Delta T}$$

For an ideal gas, pV in the definition of enthalpy, $H = U + pV$, can be replaced by nRT , and so:

$$H = U + nRT$$

$$C_p = \frac{\Delta H}{\Delta T} = \frac{\Delta U + nR \cdot \Delta T}{\Delta T} = \frac{\Delta U}{\Delta T} + nR = C_V + nR$$

For molar heat capacity:

$$C_{p,m} = C_{V,m} + R$$

Origin of Heat Capacity of Gases



Heat capacities are helpful to find the internal energy at different temperatures:

$$C_{p,m} = C_{V,m} + R$$

Monoatomic Gas (Ar)

We saw that $\frac{3}{2}RT$ was the internal energy for a monoatomic gas.

Using $\Delta U_m = \frac{3}{2}R \cdot \Delta T$:

$$C_{V,m} = \frac{\Delta U_m}{\Delta T} = \frac{\frac{3}{2}R \cdot \Delta T}{\Delta T} = \frac{3}{2}R$$

$$C_{p,m} = C_{V,m} + R = \frac{3}{2}R + R = \frac{5}{2}R$$

Origin of Heat Capacity of Gases



Linear molecules

Two degrees of rotational freedom:

$$C_{V,m} = \frac{\Delta U_m}{\Delta T} = \frac{\frac{3}{2}R \cdot \Delta T + \frac{2}{2}R \cdot \Delta T}{\Delta T} = \frac{5}{2}R$$


$$C_{p,m} = C_{V,m} + R = \frac{5}{2}R + R = \frac{7}{2}R$$

Nonlinear molecules

Three degrees of rotational freedom:

$$C_{V,m} = \frac{\Delta U_m}{\Delta T} = \frac{\frac{3}{2}R \cdot \Delta T + \frac{3}{2}R \cdot \Delta T}{\Delta T} = 3R$$

$$C_{p,m} = C_{V,m} + R = \frac{6}{2}R + R = 4R$$



	Monoatomic	Linear	Nonlinear
$C_{V,m}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{p,m}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

The Enthalpy of Physical Change



Phase changes (gas, solid, liquid) usually take place at constant pressure; the heat transfer is due to changes in enthalpy.

Intermolecular interactions

Gas \ll Liquid $<$ Solid

Enthalpy of Vaporization



The enthalpy of the phase change from liquid to gas, or vaporization, is called the vaporization enthalpy, ΔH_{vap} :

$$\Delta H_{vap} = H_{vapour} - H_{liquid}$$

The molar heat of vaporization, is the vaporization enthalpy of one mole of a substance.

For water at its boiling point, 100 °C, $\Delta H_{vap} = 40.7 \frac{\text{kJ}}{\text{mol}}$, and at 25 °C the value is $\Delta H_{vap} = 44.0 \frac{\text{kJ}}{\text{mol}}$.

This means that vaporizing 1.00 mol $\text{H}_2\text{O}(l)$ (18.02 g of water) at 25 °C and constant pressure requires 44.0 kJ of energy as heat.

Enthalpy of Vaporization



All enthalpies of vaporization are positive.

Stronger intermolecular forces, such as hydrogen bonds (*), have higher enthalpies of vaporization.

Stronger intermolecular interactions have a deeper potential energy plot.

	T_m / K	T_b / K	$\Delta H_{fus} / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_{vap} / \text{kJ}\cdot\text{mol}^{-1}$
Argon (Ar)	83.8	87.3	1.2	6.5
Methane (CH_4)	90.7	112	0.94	8.2
Acetone (CH_3COCH_3)	178	329	5.72	29.1
Methanol* (CH_3OH)	175	338	3.16	35.3
Ammonia* (NH_3)	195	240	5.65	23.4
Water* (H_2O)	273	373	6.01	40.7

Enthalpy of Fusion



The enthalpy of the phase change from solid to liquid, or fusion, is called the fusion enthalpy, ΔH_{fus} :

$$\Delta H_{fus} = H_{liquid} - H_{solid}$$

The molar heat of fusion for water at 0.0 °C is $\Delta H_{fus} = 6.0 \frac{\text{kJ}}{\text{mol}}$:

To melt 1.0 mol $\text{H}_2\text{O}(\text{s})$ (18 g of ice) at 0.0 °C, we have to supply 6.0 kJ of heat.

Vaporizing water takes much **more energy** (more than $40 \text{ kJ}\cdot\text{mol}^{-1}$), because the vaporization of a gas, requires its molecules to be separated completely, and E_{kin} to be increased dramatically. In **melting**, the molecules stay close together, and so the forces of **attraction and repulsion are almost as strong** as in the solid.

Enthalpy of Freezing



Freezing is the phase change from liquid to solid.

Enthalpy is a state function:

$$\Delta H_{\text{reverse process}} = -\Delta H_{\text{forward process}}$$

Since the enthalpy of fusion of water at 0.0°C is 6.0 kJ·mol⁻¹ the enthalpy of freezing for water at 0.0°C is -6.0 kJ·mol⁻¹.

Enthalpy of Condensation



Condensation is the change from vapour to liquid. So, this process is the reverse of ΔH_{vap} .

For water at boiling, 100 °C, $\Delta H_{vap} = 40.7 \frac{\text{kJ}}{\text{mol}}$, therefore:

$$\Delta H_{condensation} = -\Delta H_{vap} = -40.7 \frac{\text{kJ}}{\text{mol}}$$

Enthalpy of Sublimation and Deposition



Sublimation is the direct conversion of a solid into its vapor.

$$\Delta H_{\text{sublimation}} = H_{\text{vapour}} - H_{\text{solid}}$$

Frost disappears on a cold, dry morning as the ice sublimates directly into water vapour. Solid carbon dioxide also sublimates, which is why it is called “dry ice”.

Deposition is the reverse of sublimation: a vapour is converted into its solid.

$$\Delta H_{\text{deposition}} = H_{\text{solid}} - H_{\text{vapour}} = -\Delta H_{\text{sublimation}}$$

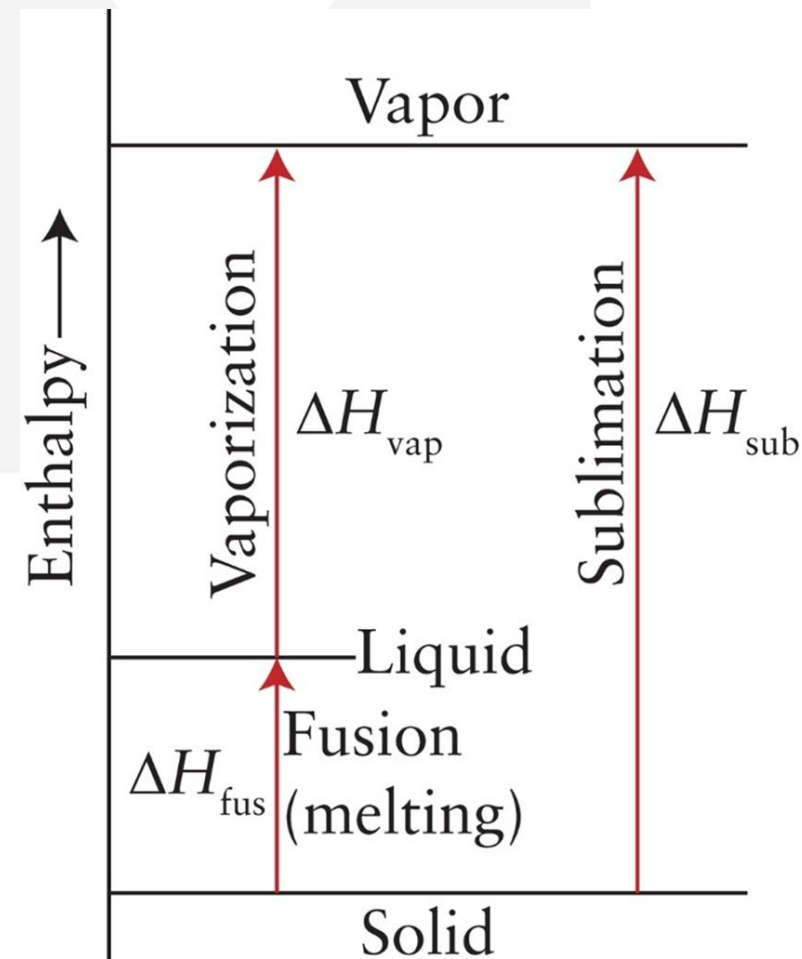


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Heating Curves

A heating curve shows the variation in the temperature of a heated sample.

As a sample of ice is heated the temperature rises steadily.

1. In a solid the molecules are still locked together as they oscillate vigorously around their mean positions.
2. As the temperature rises, reaching the melting point, the molecules have enough energy to move past one another, overcoming the attractive forces between molecules.

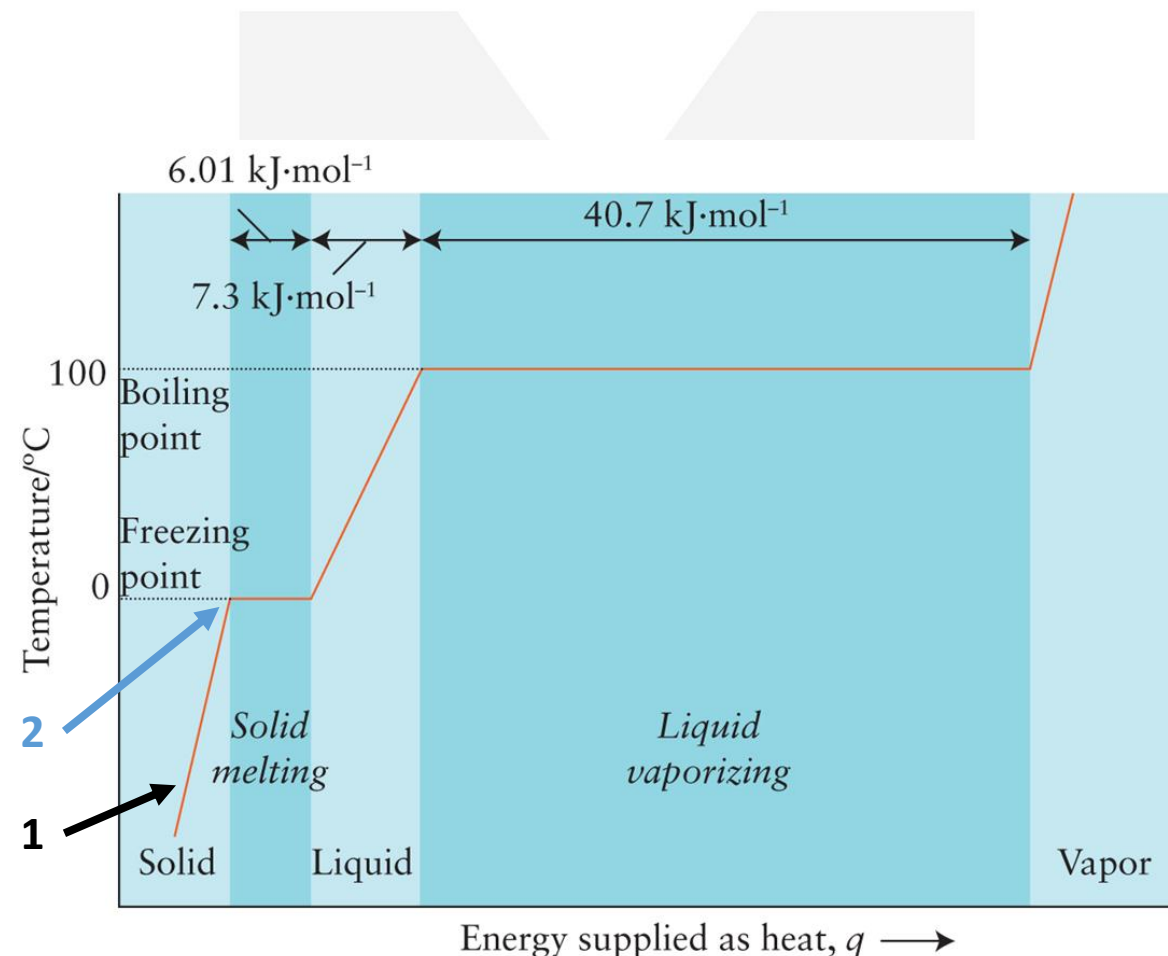


Figure 4C.9

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Heating Curves

- At this temperature, all the added energy is used to break all the attractive forces; the temperature remains constant at the melting point until all the ice has melted.
- Only then does the temperature rise again, and the rise continues right up to the boiling point.
- At the boiling point, the temperature rises again and comes to a halt.
- Now the water molecules have enough energy to escape into the vapour state, and all the heat supplied is used to form the vapor.
- After the sample has evaporated and heating continues, the temperature of the vapour rises again.

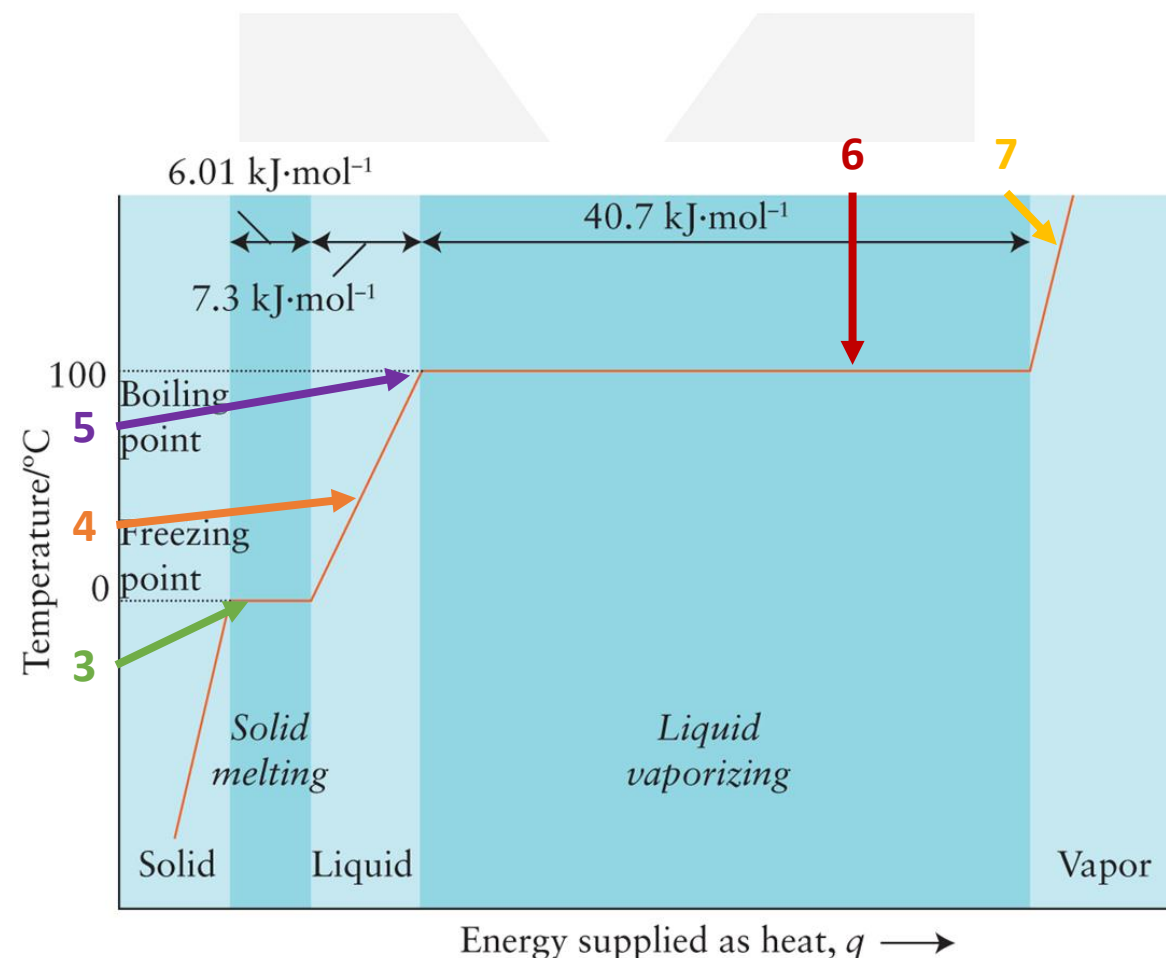


Figure 4C.9

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Heating Curves

A. The steeper the slope, the lower the heat capacity. Both the solid and vapour phases have steeper slopes than liquid, so the liquid has a greater heat capacity.

B. The liquid's high heat capacity is due largely to loose intermolecular hydrogen bonds that can take up more energy than the stiff chemical bonds between atoms found in the solid.

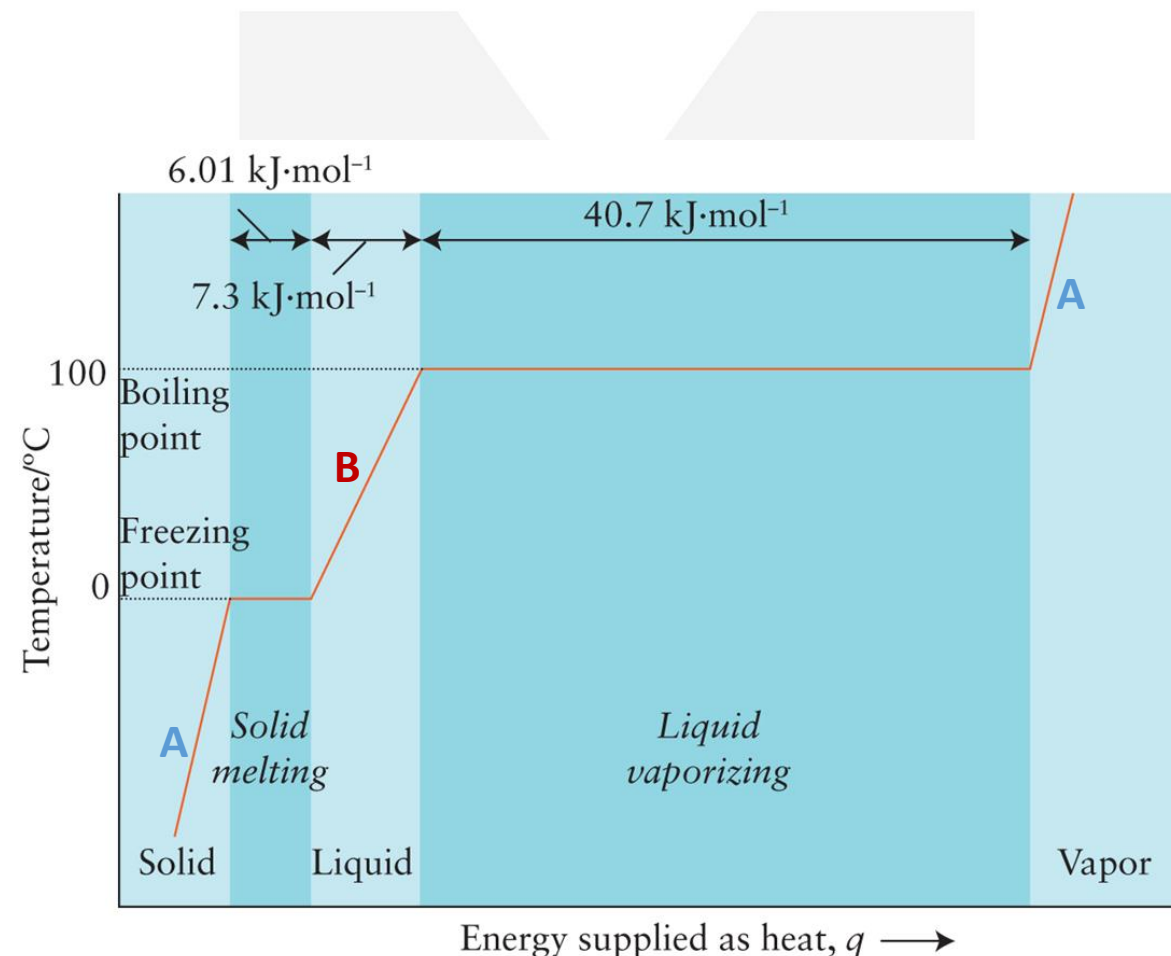


Figure 4C.9

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Example



Use the following information to construct a heating curve for bromine, Br_2 , from $-7.2\text{ }^{\circ}\text{C}$ to $70.0\text{ }^{\circ}\text{C}$.

The molar heat of fusion for bromine is $75.69\text{ kJ}\cdot\text{mol}^{-1}$ and that of vaporization is $36.02\text{ kJ}\cdot\text{mol}^{-1}$. For bromine the specific heat capacity of the vapour is $0.225\text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ and of that of the liquid is $0.473\text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$. Bromine melts at $-7.2\text{ }^{\circ}\text{C}$ and boils at $58.78\text{ }^{\circ}\text{C}$. Also calculate the energy to **heat up** 10.0 g of bromine, Br_2 , from $-7.2\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$. The molar mass of bromine is $159.8\text{ g}\cdot\text{mol}^{-1}$.

$$\Delta H_{fus, \text{Br}_2} = 75.69 \frac{\text{kJ}}{\text{mol}}$$

$$C_{s,g, \text{Br}_2} = 0.225 \frac{\text{J}}{\text{g}\cdot\text{K}}$$

$$T_{m, \text{Br}_2} = -7.2\text{ }^{\circ}\text{C}$$

$$\Delta H_{vap, \text{Br}_2} = 36.02 \frac{\text{kJ}}{\text{mol}}$$

$$C_{s,l, \text{Br}_2} = 0.4735 \frac{\text{J}}{\text{g}\cdot\text{K}}$$

$$T_{b, \text{Br}_2} = 58.78\text{ }^{\circ}\text{C}$$

Example



$$T_{m,Br_2} = -7.2\text{ }^{\circ}\text{C}$$

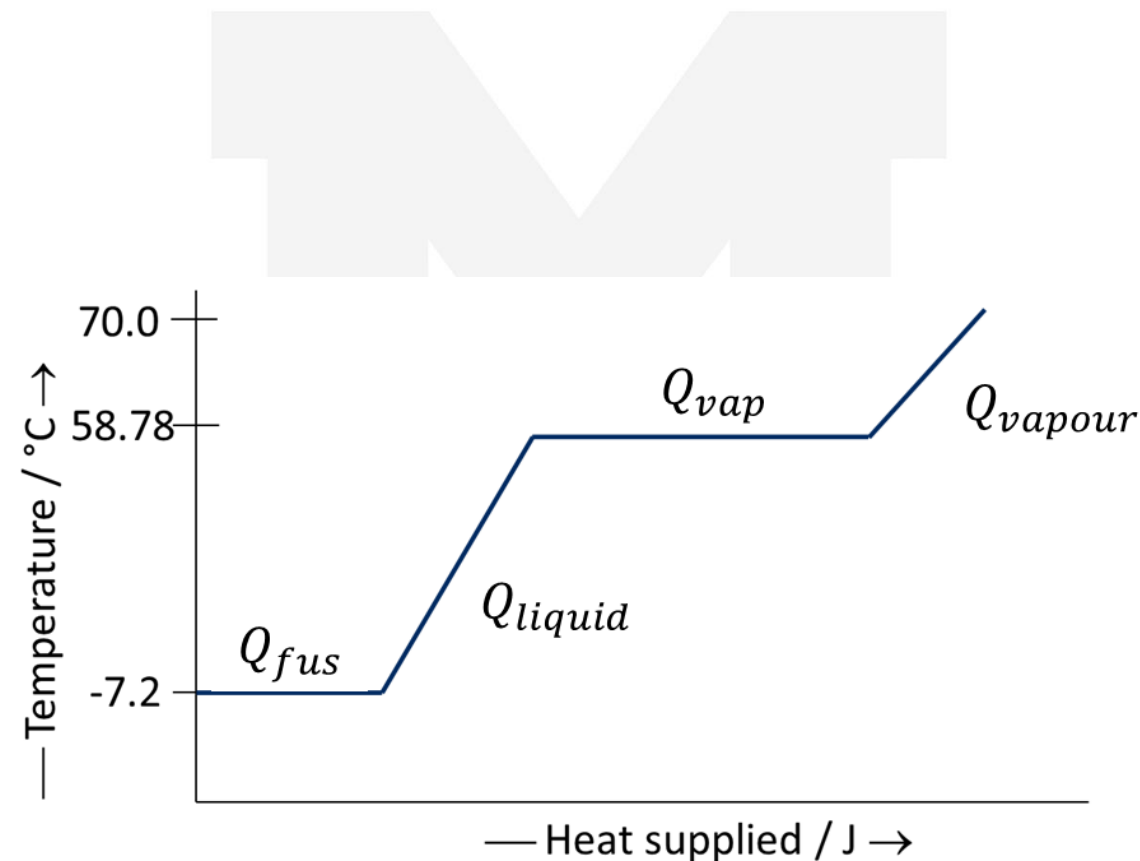
$$\Delta H_{fus,Br_2} = 75.69\text{ }\frac{\text{kJ}}{\text{mol}}$$

$$C_{s,l,Br_2} = 0.4735\text{ }\frac{\text{J}}{\text{g}\cdot\text{K}}$$

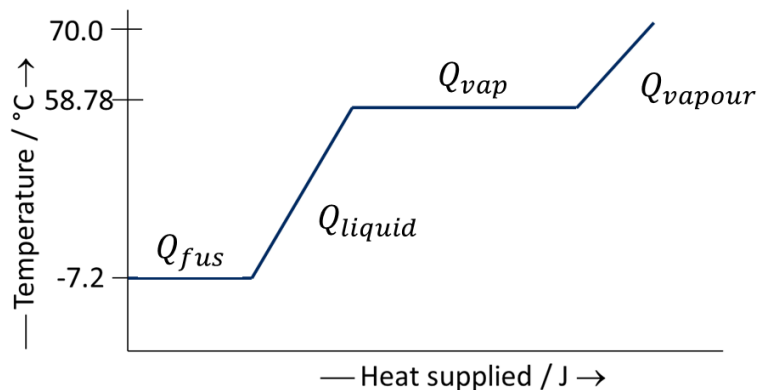
$$T_{b,Br_2} = 58.78\text{ }^{\circ}\text{C}$$

$$\Delta H_{vap,Br_2} = 36.02\text{ }\frac{\text{kJ}}{\text{mol}}$$

$$C_{s,g,Br_2} = 0.225\text{ }\frac{\text{J}}{\text{g}\cdot\text{K}}$$



Example



$$Q_{total} = Q_{fus} + Q_{liquid} + Q_{vap} + Q_{vapour}$$

$$Q_{fus} = \Delta H_{fus, Br_2} \cdot \frac{m_{Br_2}}{M_{Br_2}}$$
$$Q_{fus} = 75.69 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \frac{10.0 \text{ g}}{159.8 \frac{\text{g}}{\text{mol}}} = 4740 \text{ J}$$

$$Q_{liquid} = C_{s,l, Br_2} \cdot m_{Br_2} \cdot \Delta T$$
$$Q_{liquid} = 0.4735 \frac{\text{J}}{\text{g} \cdot \text{K}} \times 10.0 \text{ g} \times (58.78 \text{ °C} - (-7.2 \text{ °C})) = 312 \text{ J}$$

$$Q_{vap} = \Delta H_{vap, Br_2} \cdot \frac{m_{Br_2}}{M_{Br_2}}$$
$$Q_{vap} = 36.02 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \frac{10.0 \text{ g}}{159.8 \frac{\text{g}}{\text{mol}}} = 2250 \text{ J}$$

$$Q_{vapour} = C_{s,g, Br_2} \cdot m_{Br_2} \cdot \Delta T$$
$$Q_{vapour} = 0.225 \frac{\text{J}}{\text{g} \cdot \text{K}} \times 10.0 \text{ g} \times (70.0 \text{ °C} - 58.78 \text{ °C}) = 25.2 \text{ J}$$

$$Q_{total} = 4740 \text{ J} + 312 \text{ J} + 2250 \text{ J} + 25.2 \text{ J} = 7330 \text{ J}$$

$$m_{Br_2} = 10.0 \text{ g}$$
$$M_{Br_2} = 159.8 \frac{\text{g}}{\text{mol}}$$
$$T_{m, Br_2} = -7.2 \text{ °C}$$
$$\Delta H_{fus, Br_2} = 75.69 \frac{\text{kJ}}{\text{mol}}$$
$$C_{s,l, Br_2} = 0.4735 \frac{\text{J}}{\text{g} \cdot \text{K}}$$
$$T_{b, Br_2} = 58.78 \text{ °C}$$
$$\Delta H_{vap, Br_2} = 36.02 \frac{\text{kJ}}{\text{mol}}$$
$$C_{s,g, Br_2} = 0.225 \frac{\text{J}}{\text{g} \cdot \text{K}}$$



Enthalpy of Chemical Changes



Enthalpy of Chemical Changes

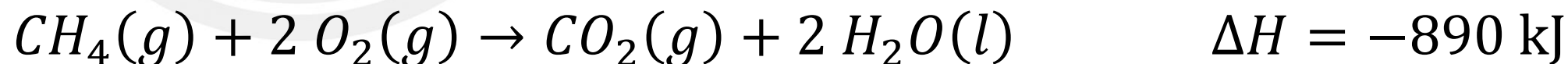


We have seen enthalpy changes in phase changes. The same principles apply to chemical changes.

Knowing enthalpies of a chemical change helps us determine which are good fuels, or to study biochemical processes.

Every chemical reaction is accompanied by energy transfer as heat.

Combustion of methane, the major component of natural gas. From calorimetry experiments we know the heat and write:



Enthalpy of Chemical Changes



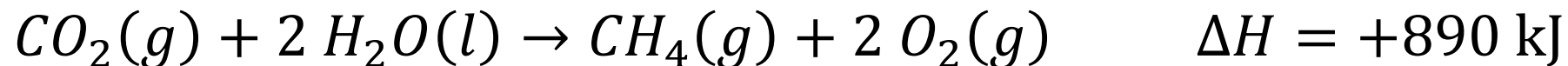
The stoichiometric coefficients corresponding to an enthalpy change:

1 mol $\text{CH}_4(g)$ and 890 kJ of heat, for instance.

If the same reaction is **multiplied by 2**, then the change in enthalpy will be twice as great:



For the **reverse** reaction we write:



The Relation between ΔH and ΔU



We have measured heat with a bomb calorimeter.

At constant volume, the heat transfer is $Q = \Delta U$; $C_{V,m} = \frac{\Delta U}{\Delta T}$

At constant pressure, it is $Q = \Delta H$; $C_{p,m} = \frac{\Delta U}{\Delta T} + R$

However, it is sometimes necessary to convert the measured value of ΔU into ΔH .

For example, it is **easy** to measure the heat released by the combustion of **glucose** in a **bomb calorimeter**, but to use that information in studying the metabolism, which takes place at constant pressure, we need the **enthalpy of the reaction**.

The Relation between ΔH and ΔU



For reactions in which **no gas** is generated or consumed, **little expansion work** is done. The difference between ΔH and ΔU is negligible, so we can set:

$$\Delta H = \Delta U$$

However, if a **gas is formed** in the reaction and **expansion work** is done, the difference can be **significant**.

We can use the ideal gas law to relate the values of ΔH and ΔU for gases that behave ideally.

The Relation between ΔH and ΔU



The relation between ΔH and ΔU is $H = U + pV$, or:

$$H = U + nRT$$

We suppose initial amount of reactant gas is $n_{initial}$:

$$H_{initial} = U_{initial} + pV_{initial} = U_{initial} + n_{initial}RT$$

and that after the reaction, the amount of ideal gas product molecules is n_{final} :

$$H_{final} = U_{final} + pV_{final} = U_{final} + n_{final}RT$$

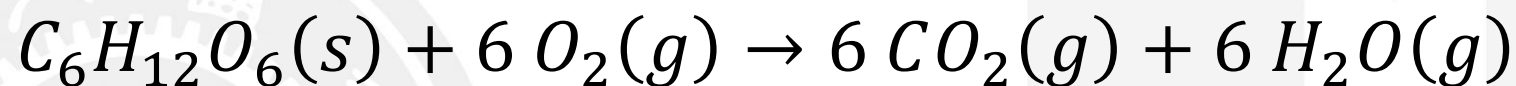
The **difference** is $\Delta H = H_{final} - H_{initial} = \Delta U + (n_{final} - n_{initial})RT$ or:

$$\Delta H = \Delta U + \Delta n_{gas}RT$$

Example



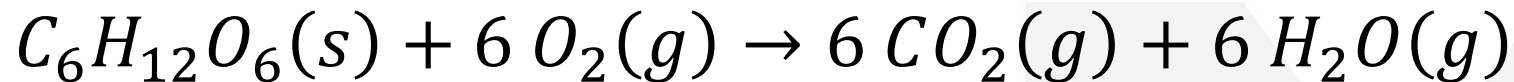
A constant-volume calorimeter showed that the heat generated by the combustion of 1.000 mol glucose molecules in the reaction



is 2559 kJ at 298 K, and so $\Delta U = -2559$ kJ.

What is the change in enthalpy for the same reaction?

Example



$$\Delta H = \Delta U + \Delta n_{gas}RT$$

$$\Delta n_{gas} = n_{final} - n_{initial} = 12 \text{ mol} - 6 \text{ mol} = +6 \text{ mol}$$

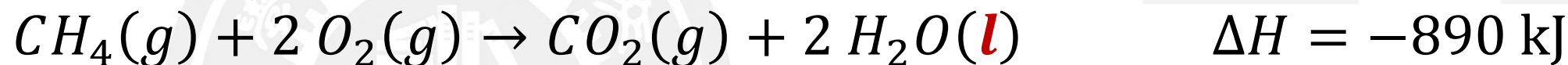
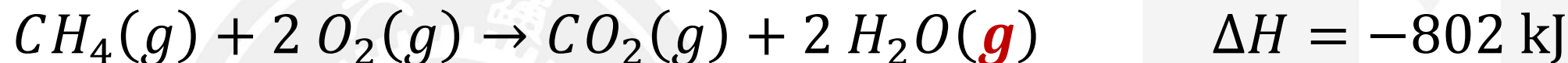
$$\Delta H = -2559 \text{ kJ} + \left(6 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \right) = -2559 \text{ kJ} + 14.9 \text{ kJ} = -2544 \text{ kJ}$$

Notice that ΔH is less negative (more positive) than ΔU for reactions that generate gases: less energy is obtained because some of the energy is used to expand to make room for the reaction products.

Standard Reaction Enthalpies

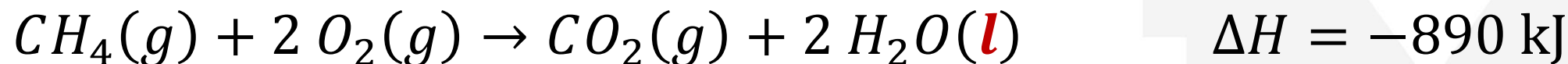
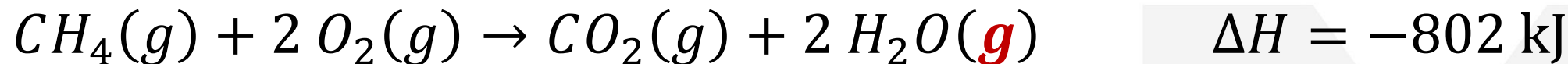


Always specify the state of each substance. For methane:



The difference between $H_2O(g)$ and $H_2O(l)$ is 88 kJ of energy. So, for transforming just one mole of $H_2O(g)$ to $H_2O(l)$, $\Delta H_{vap} = 44.0 \frac{\text{kJ}}{\text{mol}}$.

Standard Reaction Enthalpies



For the oxidation of methane to $\text{H}_2\text{O}(l)$, $\Delta H^\circ = -890 \text{ kJ}$. The heat output of 890 kJ indicates that 1 mol $\text{CH}_4(g)$ as pure methane gas at 1 bar is allowed to react with pure oxygen gas at 1 bar to produce 1 mole $\text{CO}_2(g)$ and two moles of $\text{H}_2\text{O}(l)$ under standard state conditions (298.15 K, 10^5 Pa).

Standard state meaning the reaction took place at exactly 1 bar and 298.15 K. Not to be confused with Standard Temperature and Pressure (STP, 273.15 K, 10^5 Pa) or Standard Ambient Temperature and Pressure (SATP, 298.15 K, 1 atm).

Enthalpy is a state function; therefore, the value of ΔH is independent of the path between given initial and final states.

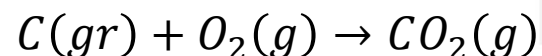
Hess's law:

The overall reaction enthalpy is the **sum** of the reaction enthalpies of each step.

Combining Reaction Enthalpies: Hess's Law

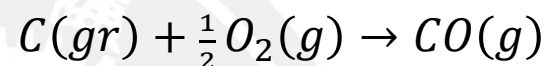


The oxidation of carbon as graphite, denoted $C(gr)$, to carbon dioxide:



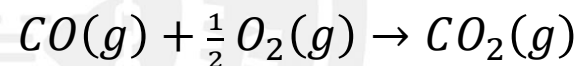
This can be thought of as two different steps.

One step is the oxidation of carbon to carbon monoxide:



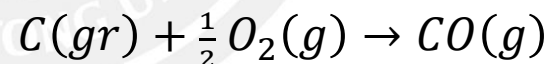
$$\Delta H^\circ = -110.5 \text{ kJ}$$

The second step is the oxidation of CO to CO_2 :

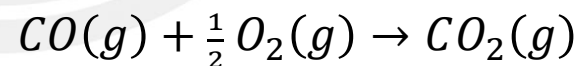


$$\Delta H^\circ = -283.0 \text{ kJ}$$

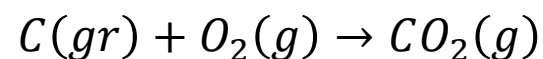
We can sum the previous two reaction to find our desired reaction:



$$\Delta H^\circ = -110.5 \text{ kJ}$$



$$\Delta H^\circ = -283.0 \text{ kJ}$$



$$\Delta H^\circ = -393.5 \text{ kJ}$$

Combining Reaction Enthalpies: Hess's Law



Hess's law is a way to find unknown enthalpies:

1. Select one of the reactants in the overall reaction and write down a chemical equation in which it also appears as a reactant.
2. Select one of the products in the overall reaction and write down a chemical equation in which it also appears as a product.
3. Cancel unwanted species in the sum.
4. Once the sequence is complete, combine the standard reaction enthalpies.

Note: Reversing the equation changes the sign of enthalpy. If multiplying the stoichiometric coefficients by a factor, multiply the reaction enthalpy by the same factor.

Standard Enthalpies of Formation



It is impractical to list every standard reaction enthalpy. However, chemists have devised an ingenious alternative.

- First, they report the **standard enthalpies of formation** of substances per one mole.
- Then they **combine these quantities** to obtain the standard enthalpy of reaction needed.

Enthalpies under standard state conditions for $\text{C}(\text{gr})$, $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ are all 0.

Substance	$\Delta H_f^\circ / \text{kJ}\cdot\text{mol}^{-1}$ (@298.15 K, 10^5 Pa)
Ammonia ($\text{NH}_3(\text{g})$)	-46.11
Nitrogen dioxide ($\text{NO}_2(\text{g})$)	+33.18
Water ($\text{H}_2\text{O}(\text{l})$)	-285.83
Water ($\text{H}_2\text{O}(\text{g})$)	-241.82
Graphite ($\text{C}(\text{gr})$)	0
Hydrogen ($\text{H}_2(\text{g})$)	0
Oxygen ($\text{O}_2(\text{g})$)	0

Standard Enthalpies of Formation

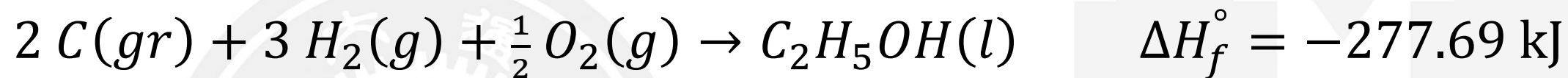


The standard enthalpy of formation, ΔH_f° , is the change in enthalpy for forming the element or molecule in its standard state (298.15 K, 10^5 Pa, physical state) per ***one mole***.

Standard Enthalpies of Formation



The standard enthalpy of formation, ΔH_f° , of a substance is the standard reaction enthalpy per mole of formula units for the formation of a substance from its **elements in their most stable form**, as in the reaction.



Standard enthalpies of formation are expressed **per one mole** of molecules, as in $-277.69 \frac{\text{kJ}}{\text{mol}}$, meaning that mole is a unit.

The standard enthalpy **of forming** 1 mol $C_2H_5OH(l)$ is -277.69 kJ.

Standard Reaction Enthalpy

First, calculate the reaction enthalpy for the formation of all products.

Second, calculate the reaction enthalpy for all reactants.

The difference between these two totals is the standard enthalpy of the reaction.

$$\Delta H_{\text{reaction}}^{\circ} = \sum (n \cdot \Delta H_{f,\text{products}}^{\circ}) - \sum (n \cdot \Delta H_{f,\text{reactants}}^{\circ})$$

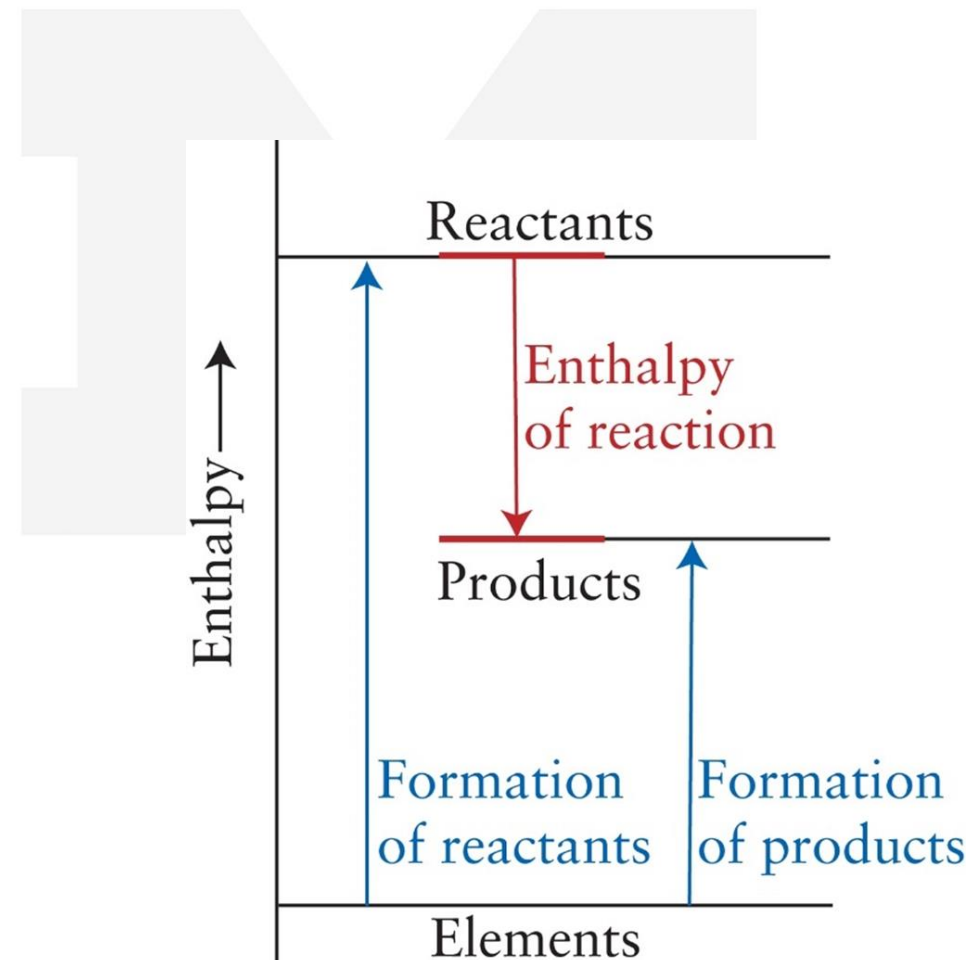


Figure 4D.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Suppose we know the reaction enthalpy for one temperature but require it for another temperature.

For instance, the temperature of the human body is about 37 °C, but the data in Appendix 2A in the textbook are for 25 °C.

Does an increase of 12 °C make much difference to the reaction enthalpy of a metabolic process?

Variation of Reaction Enthalpy With Temperature



The enthalpies of both reactants and products increase with temperature.

The increase in enthalpy depends on the heat capacity at constant pressure, and it is easy to deduce using Kirchhoff's law.

$$\Delta H_{T_2} = \Delta H_{T_1} + (T_2 - T_1) \cdot \Delta C_p$$

$$\Delta C_p = \sum (n \cdot C_{p,m,products}) - \sum (n \cdot C_{p,m,reactants})$$

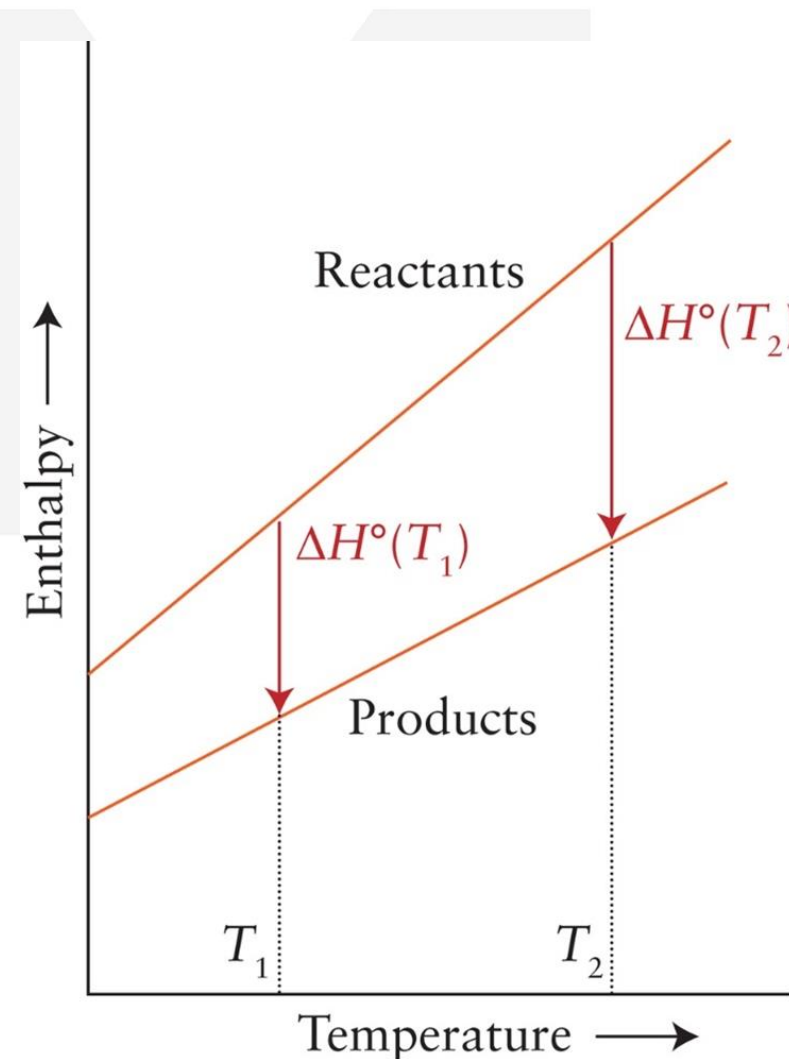


Figure 4D.6

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The Born-Haber Cycle



Earlier we calculated energy changes in an ionic system to find lattice energy.

The difference in molar enthalpy of solid and gas is called the lattice enthalpy of the solid, ΔH_L .

The lattice enthalpy of a solid cannot be measured directly.

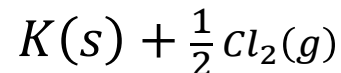
Instead, we measure it indirectly by using an application of Hess's law.

The procedure uses a **Born-Haber cycle**, a closed path of steps.

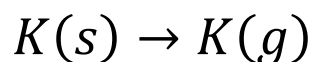
Lattice Energy of KCl



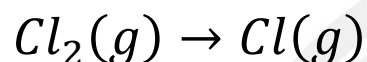
Begin with the pure elements:



1. Atomize them to form gaseous atoms,

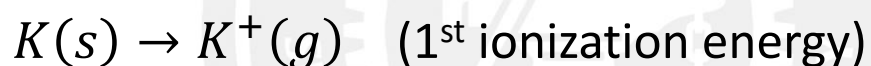


$$\Delta H_f^\circ = +89 \frac{\text{kJ}}{\text{mol}}$$

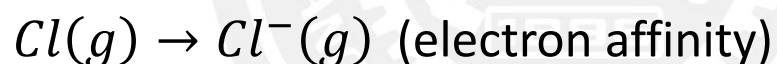


$$\Delta H_f^\circ = +122 \frac{\text{kJ}}{\text{mol}}$$

2. Ionize the atoms to form gaseous ions,

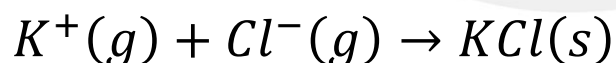


$$\Delta H_f^\circ = +418 \frac{\text{kJ}}{\text{mol}}$$



$$\Delta H_f^\circ = -349 \frac{\text{kJ}}{\text{mol}}$$

3. Allow the ions to form an ionic solid,



$$\Delta H_f^\circ = -\Delta H_L$$

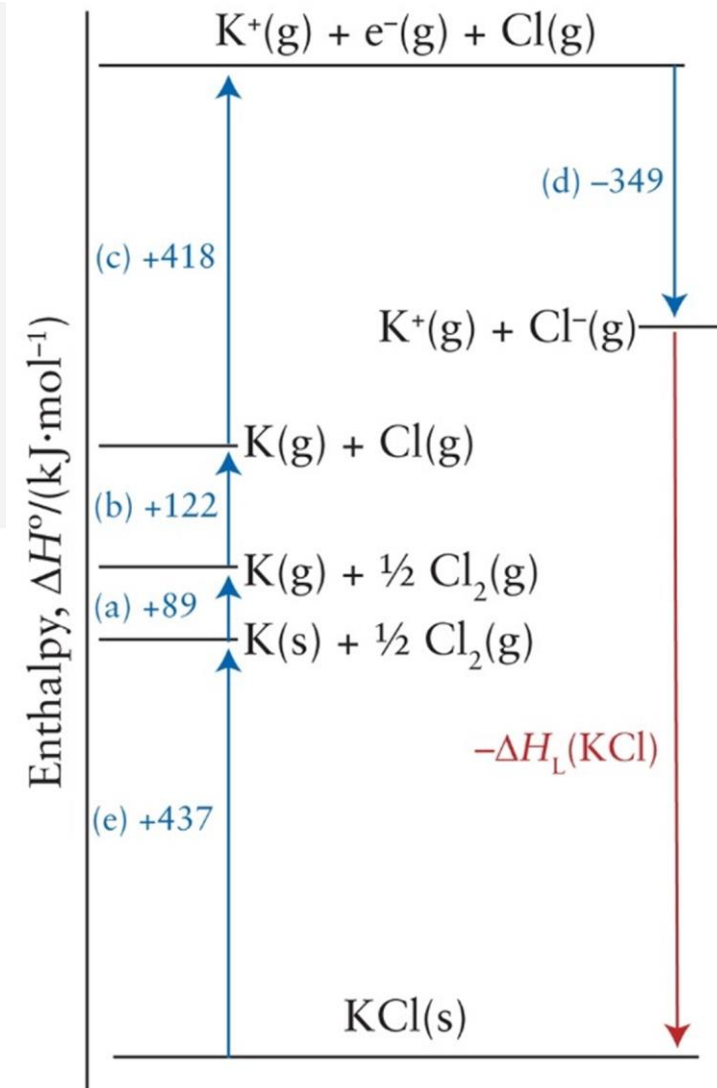


Figure 4E.2

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Lattice Energy of KCl



4. Then convert the solid back into the pure elements.



Note that the sign is “-” because the reaction is reversed.

All steps together add up to 0.

$$+89 \frac{\text{kJ}}{\text{mol}} + 122 \frac{\text{kJ}}{\text{mol}} + 418 \frac{\text{kJ}}{\text{mol}} + \left(-349 \frac{\text{kJ}}{\text{mol}}\right) + (-\Delta H_L) + 437 \frac{\text{kJ}}{\text{mol}} = 0$$

$$\Delta H_L = +717 \frac{\text{kJ}}{\text{mol}}$$

Note: Lattice energies describe the dispersion of a crystal into gaseous ions and are therefore **always positive**.

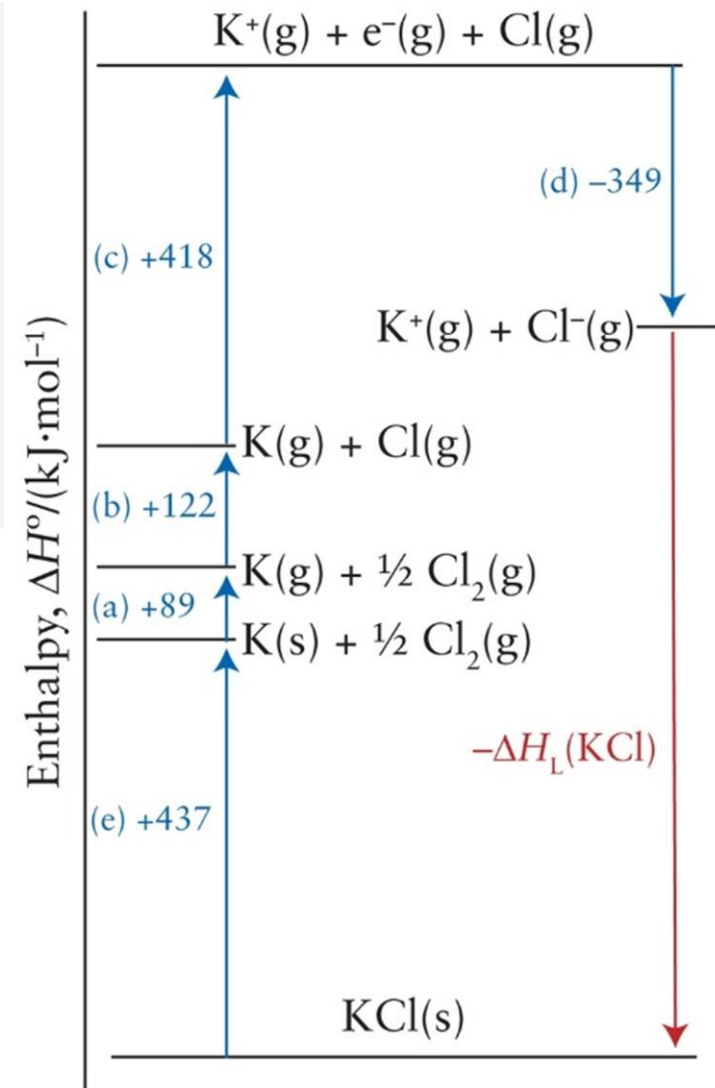


Figure 4E.2

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Bond Enthalpies



In chemical reactions, old bonds break and new bonds form.

Bond strengths are measured with bond enthalpies, ΔH_B .

Changes in standard molar enthalpies of a product and reactant for H_2 ,



We write $\Delta H_B^\circ(H-H) = 436 \frac{\text{kJ}}{\text{mol}}$ to report this value and conclude that 436 kJ of heat is needed to dissociate 1 mol $H_2(g)$ into atoms.

Positive enthalpies means heat is required to break a bond; bond breaking is always endothermic and bond formation is always exothermic.