

Chemical Principles

8. Thermodynamics

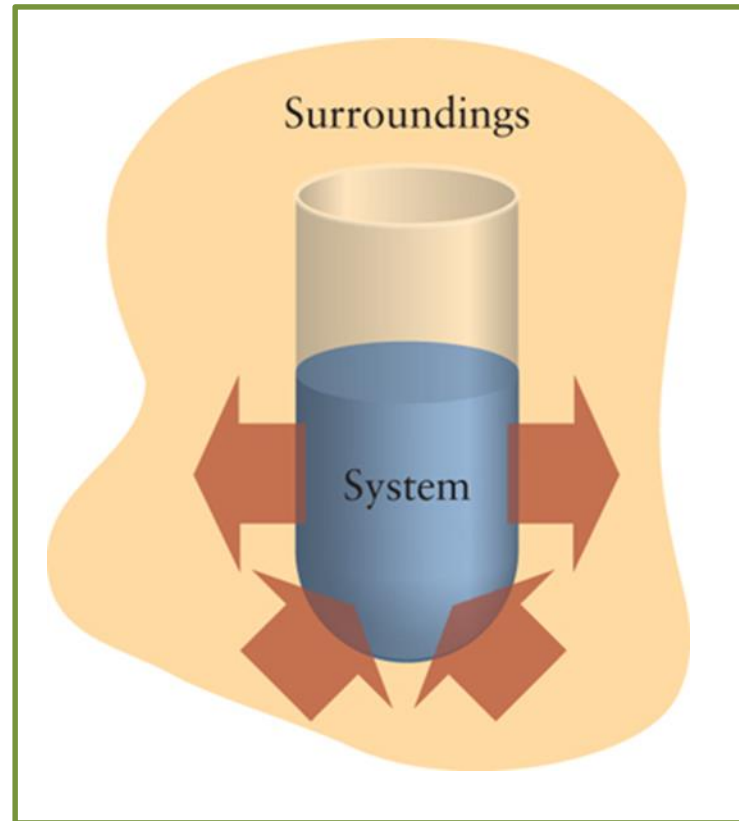
The first Law

Thermodynamics Laws

- The first law of thermodynamics is about **Energy Conservation**, in terms of **work** or **heat**;
- The second law of thermodynamics explains why some chemical reactions take place and others do not.
- The third law is statistical mechanics, calculating what we learn in the 2nd law;

Systems, Surroundings and Universe

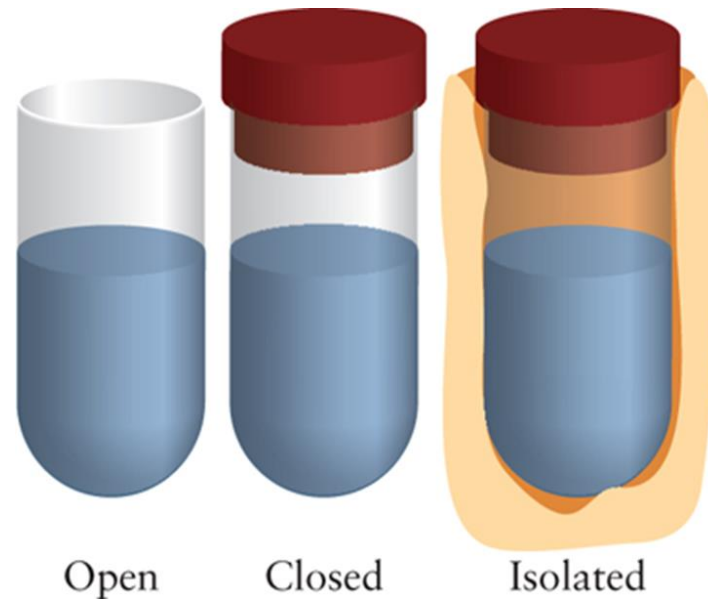
The **system** and the **surroundings** jointly make up the **universe**.



Universe

The universe consists of a system and its surroundings.

An **open system** can exchange both matter and energy with the surroundings,



Isolated systems have no contact with its surroundings. A sealed, insulated, rigid container.

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

- Expansion work is associated with change in volume.
e.g. a gas expands in a cylinder pushing a piston against the atmosphere
- Non-expansion work is a work without volume change
e.g. chemical reactions do nonexpansive work by causing electrical current to flow

Expansion Work:

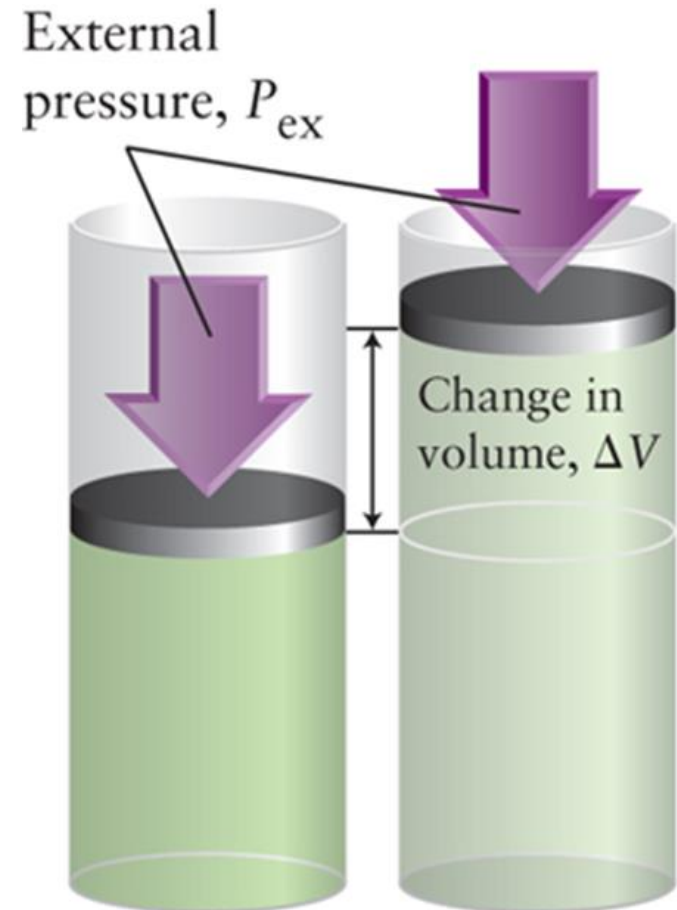
Work = opposing force \times distance moved

The **expansion work** done by the system is opposite of the ΔV , against the external pressure P_{ex}

$$W = - P_{\text{ex}} \Delta V$$

If $\Delta V > 0$ (expansion), the work is **negative**.

Free expansion: $P_{\text{ex}} = 0$, then $W = 0$.



Reversible Process

In thermodynamics, a **reversible** process is one that can be reversed by an **infinitely small change** in a variable.

For example, if the pressures of inside or outside of a piston are equal, the system may be increases or decreases infinitesimally.

The concept of reversible process is of the greatest importance in thermodynamics.

Measuring isothermal work with changing external pressure

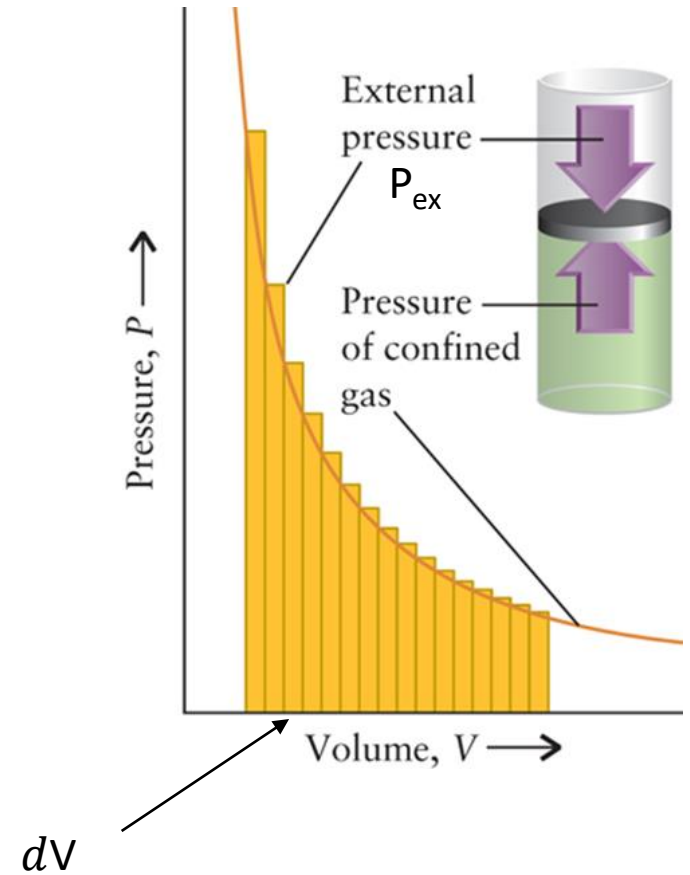
Isothermal means temperature remains unchanged.

The simplest **reversible** change is infinitesimal change in volume, then

$$dw = -P_{\text{ex}}dV$$

Matching external to the internal pressure, $P = P_{\text{ex}}$

$$dw = -PdV$$



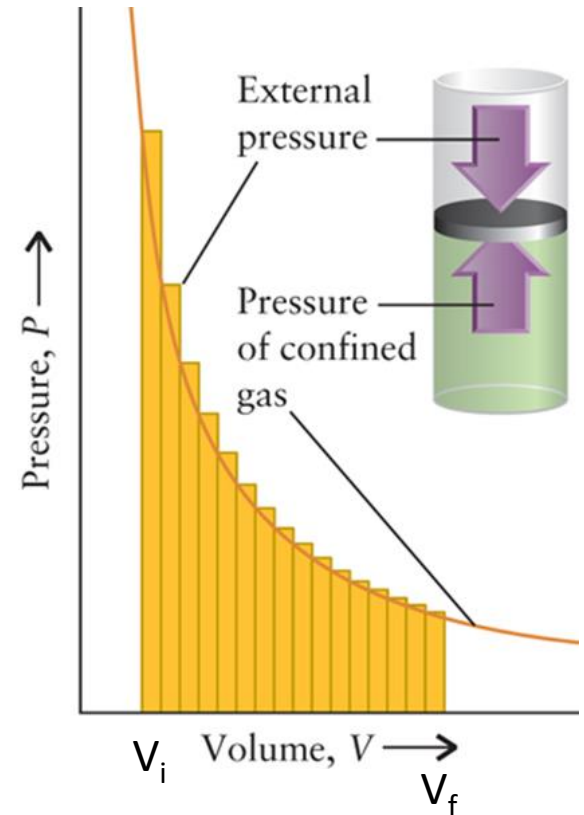
Calculating isothermal work with changing external pressure

For an ideal gas, $PV = nRT$, we have

$$dw = \frac{nRT dV}{V}$$

If the volume change from V_i to V_f ,

$$w = -nRT \ln \frac{V_f}{V_i}$$



The work is the area under the isothermal line from V_i to V_f

Heat

In thermodynamics, heat (q) is the energy transferred as a result of a temperature difference.

Heat capacity measures how much heat is transferred to increase one degree of temperature.

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

Specific heat and heat capacity

Specific heat is heat per degree per gram.

Heat capacity is heat per degree and per mole.

TABLE 7.2 Specific and Molar Heat Capacities of Common Materials*

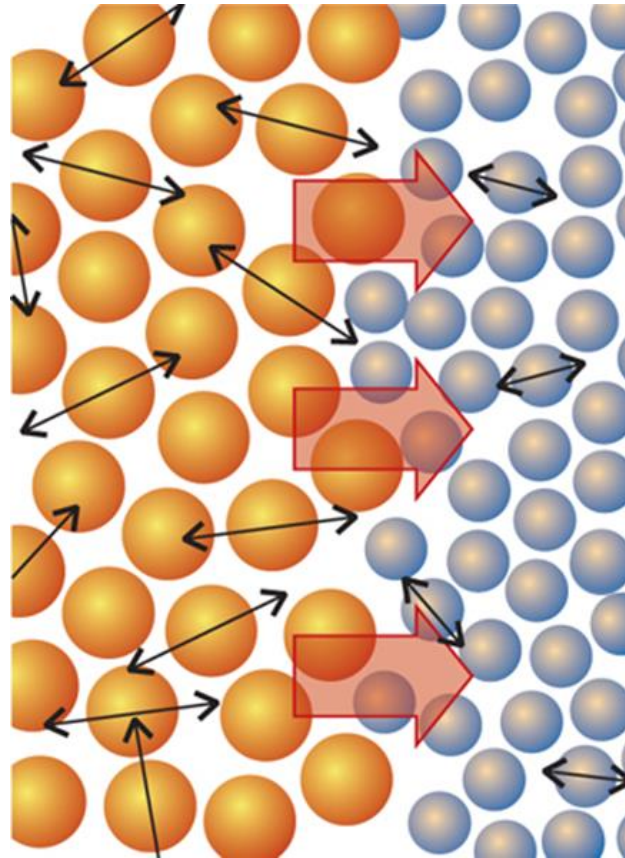
Material	Specific heat capacity ($\text{J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1}$)	Molar heat capacity ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
air	1.01	—
benzene	1.05	136
brass	0.37	—
copper	0.38	33
ethanol	2.42	111
glass (Pyrex)	0.78	—
granite	0.80	—
marble	0.84	—
polyethylene	2.3	—
stainless steel	0.51	—
water: solid	2.03	37
liquid	4.184	75
vapor	2.01	34

*More values are available in Appendices 2A and 2D; values assume constant pressure. Specific heat capacities commonly use Celsius degrees in their units, whereas molar heat capacities commonly use kelvins. All values except that for ice are for 25°C.

Molecular level of heat

The direction of
heat transfer. →

Hot, fast
moving
particles.



Cold, slow
moving
particles.

At the atomic level, the **heat** is transferred due to the **kinetic** energy transfers.

Energy transfer as Heat: q

- If **energy leaves** the *system* as heat, the internal energy of the system decreases, and heat is negative.
- If **energy enters** a *system* as heat, the internal energy of the system increases and **q** is positive.
- In thermodynamics, negative means the system release energy or reduce its internal energy. Positive means the system gain energy or increase its internal energy.

Internal energy, U

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

Internal energy includes all kind of energies, atoms, electrons, nuclei, potential energies, kinetic energies.

Only change of internal energy is meaningful,

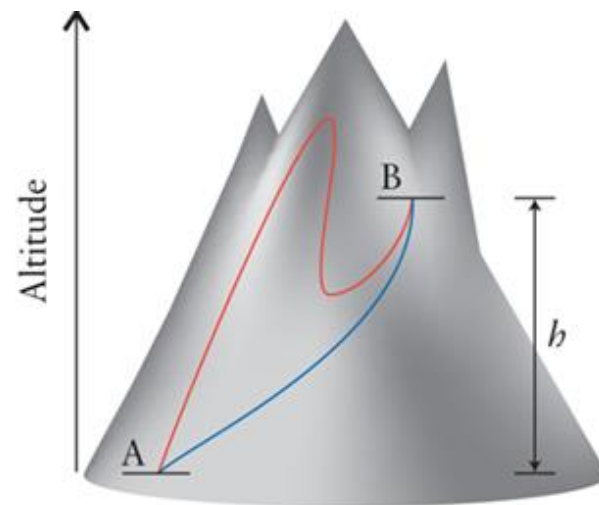
$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

Internal energy is a state function. It depends on state.

State Functions

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

A state function is like altitude on a mountain. The change in *altitude* between the two points is the same regardless of the path.



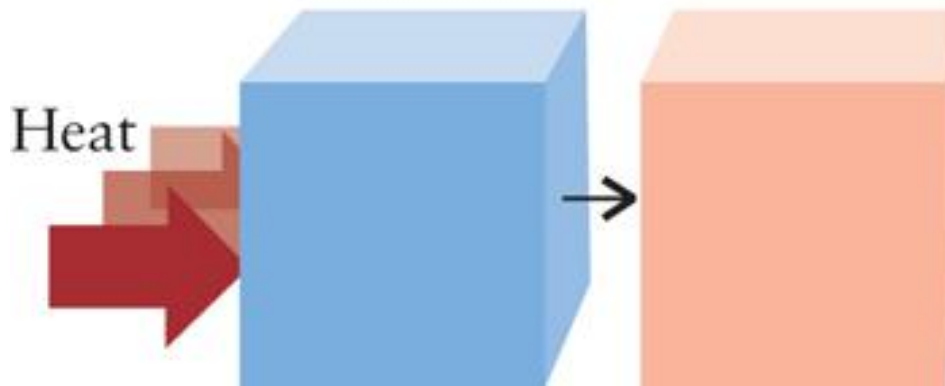
- Pressure, volume, temperature are state functions.
- Internal energy is a state function.
- Work, Heat depends on the process, they are not state functions.

The Origin of Internal Energy

Internal energy is energy stored in a system as kinetic energy (KE) and potential energy (PE).

Heating a substance always makes the molecules move faster so that they will have a higher KE.

Not immediately clear but true is that heating a substance also push the molecules to state with higher PE.



The Origin of Internal Energy

Equipartition Theorem

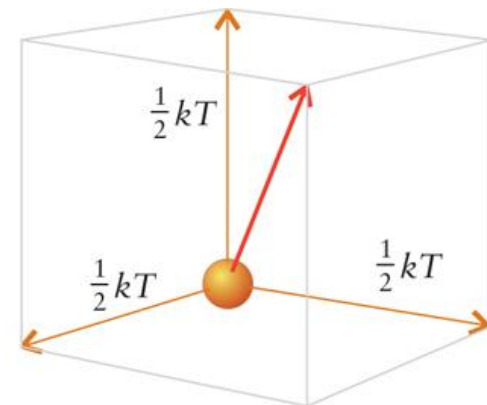
At classical limit (when energy is continuous), energy is partitioned equally over all modes of molecular motions (translation, rotation and vibration). Each mode contributes $RT/2$ in the internal energy.

This does not include the electron and nucleus energies, which can be viewed as a constant.

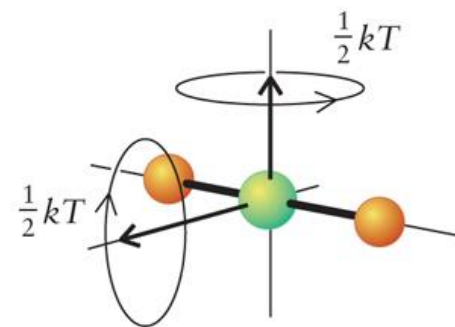
The Origin of Internal Energy

Molecule has three types of motions:

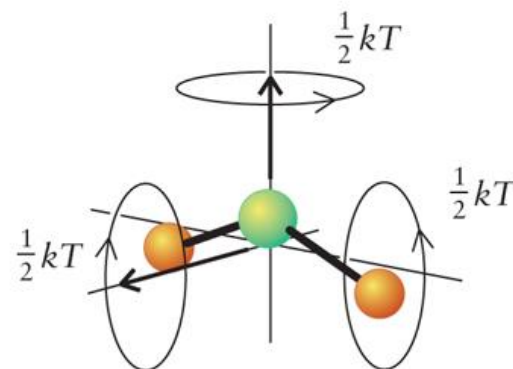
- Translation, moving through 3 dimensions; **KE** = $\frac{3}{2}RT$ or 3.72 kJ·mol⁻¹ at 25C.
- Rotation, 2 rotating motions for **linear**, **KE** = RT or 2.48 kJ·mol⁻¹, or $\frac{3}{2}RT$ for **nonlinear**;
- At high temperature, each vibration (3n-5 OR 3n-6) modes contributes **KE**= $RT/2$, **PE**= $RT/2$.



(a)



(b)



(c)

The First Law

The change of internal energy is related to heat and work by:

$$\Delta U = q + w$$

It is about the energy conservation. The energy can be transferred either by heat or by work, or by both.

If the system release energy ($q < 0$ or $w < 0$), its internal energy decreases $\Delta U < 0$.

If the system gain energy ($q > 0$ or $w > 0$), its internal energy increases $\Delta U > 0$.

The First Law

Some circumstances:

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

$$\Delta U = 0$$

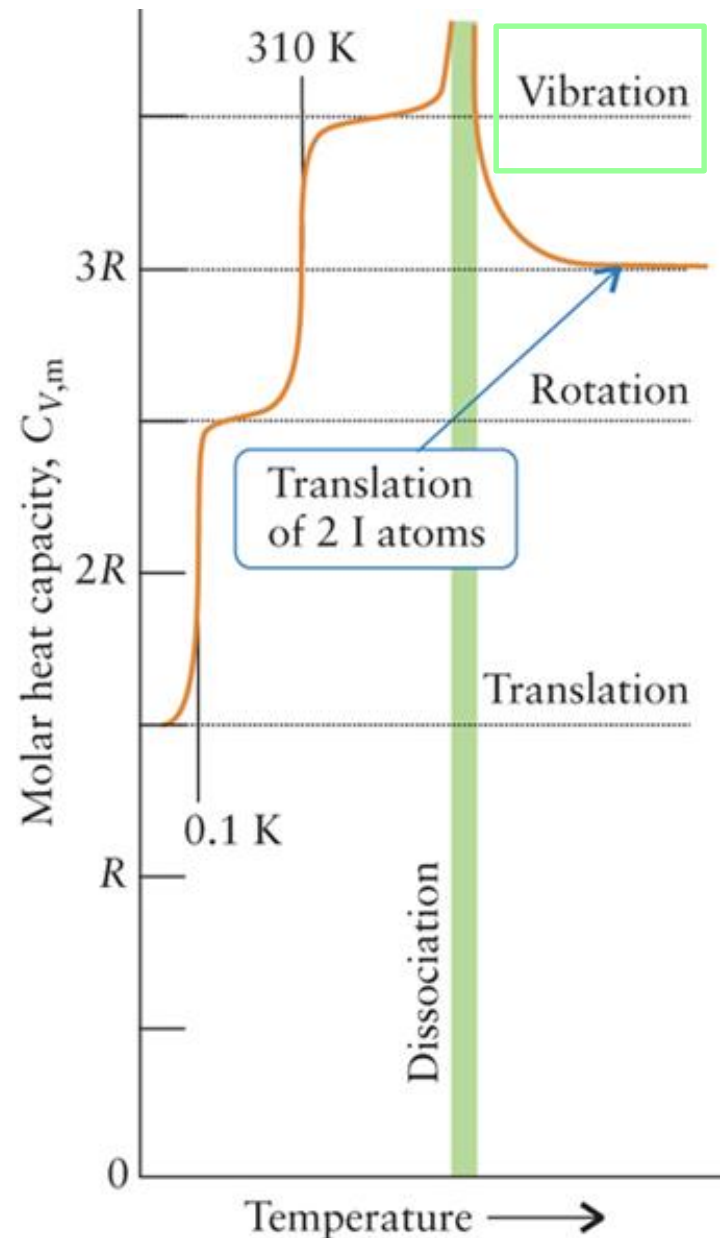
At constant volume and there is no non-expansion work ($w=0$), change of internal energy is the heat transferred

$$\Delta U = q$$

Heat capacity is called constant volume heat capacity

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

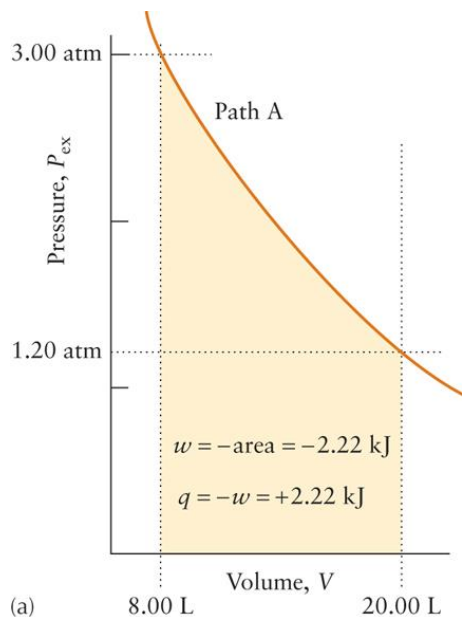
The Heat Capacities C_v of I_2 Gas



1. Because each mode of motion contributes $RT/2$ to internal energy, it contributes $R/2$ to the constant volume heat capacity (C_v).
2. The translational motion contributes to the heat capacity at very low temperature ($1.5R$).
3. Next is the contribution from rotation ($1R$)
4. Vibrations contribute only at high temperatures ($1R$).
5. The bond-break requires a lot of energy, very large C_v
6. After dissociation, two atoms, each contributes $1.5R$, the total is $3R$.

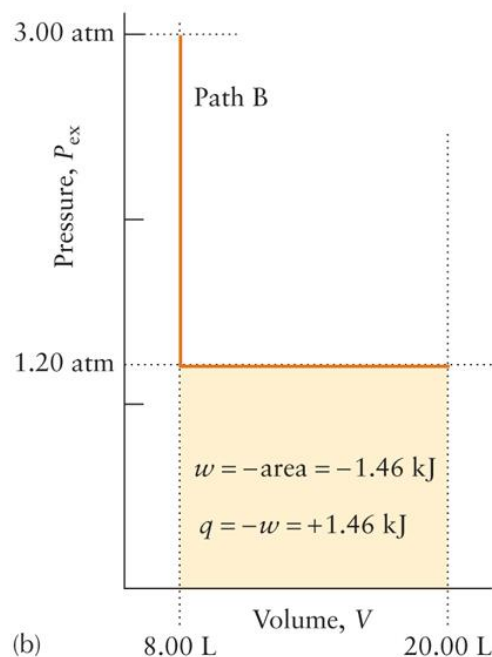
Example 1.00 mol of ideal gas molecules at 292 K and 3.00 atm expands from 8.00 L to 20.00 L by two different paths. (a) isothermal reversible expansion. (b) Two steps – reduce T to low pressure and increase temperature at constant pressure until the volume reaches 20.00 L. Calculate work, internal energy and heat transferred.

Isothermal: $w = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$



(a)

Isobaric: $w = P (V_{\text{final}} - V_{\text{initial}})$



(b)

For ideal gas, calculate the end pressure,

$$P_2 = P_1 V_1 / V_2 = 3.00 \times 8.00 / 20.00 = 1.2$$

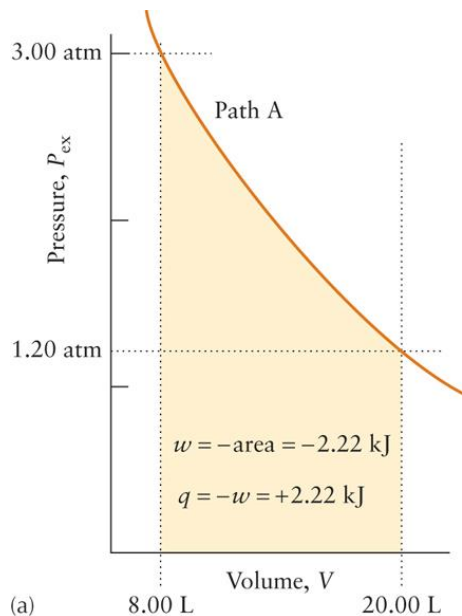
Work (w) can be calculated as follows.

Since P , V are the same, T must be the same at the end of Path B.

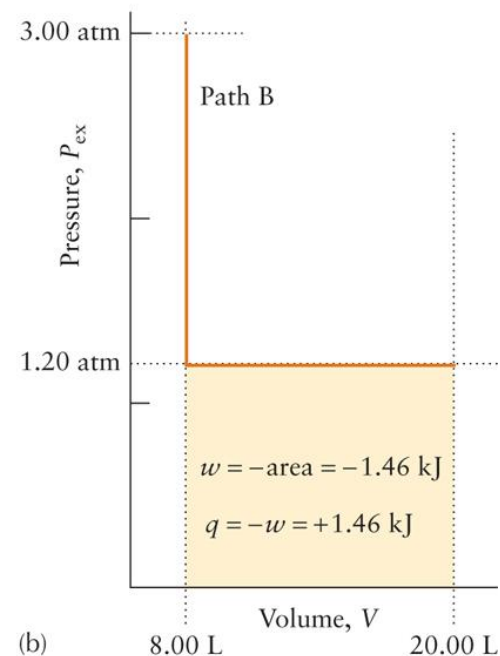
Since the energy only depends on temperature, then $\Delta U = 0$.

$\Delta U = q + w$, calculate q .

Isothermal: $w = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$



Isobaric: $w = P (V_{\text{final}} - V_{\text{initial}})$



Enthalpy

Defined as $H = U + PV$

At constant pressure:

$$\Delta H = \Delta U + P\Delta V$$

Substitute $\Delta U = q + w$, then

$$\Delta H = q + w + P\Delta V$$

Since $w = -P\Delta V$,

$$\Delta H = q - P\Delta V + P\Delta V = q$$

At constant pressure without non-expansion work

$$\Delta H = q$$

Enthalpy: $\Delta H = q$

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

We note:

that $\Delta H < 0$ for **exothermic** reactions, “-”,
whereas $\Delta H > 0$ for **endothermic** reactions, “+”.

Heat Capacities at Constant Pressure

The definition of heat capacity is $q = C \Delta T$

At **constant pressure** $\Delta H = q$

Substitute: $\Delta H = q$

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

For an **ideal gas**, $PV=nRT$, and so $H = U + nRT$

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

For **molar heat capacity** $C_{p,m} = C_{v,m} + R$

The Heat Capacities of Gases

Monoatomic Gas (3 translation):

$$C_{v,m} = \frac{\Delta U_m}{\Delta T} = \frac{3/2 R \Delta T}{\Delta T} = 3/2 R$$
$$C_{p,m} = 3/2 R + R = 5/2 R$$

Linear molecule (3 translation + 2 rotation)

$$C_{v,m} = \frac{3/2 R \Delta T + RT}{\Delta T} = 5/2 R$$
$$C_{p,m} = 5/2 R + R = 7/2 R$$

Nonlinear molecule (3 translation + 3 rotation)

$$C_{v,m} = \frac{3/2 R \Delta T + 3/2 RT}{\Delta T} = 3R$$
$$C_{p,m} = 4R$$

Example Calculate the final temperature and the change in internal energy ΔU when 500. J of energy is transferred as heat to 0.900 mol $O_2(g)$ at 298 K and 1.00 atm at (a) constant volume; (b) constant pressure. Treat the gas as ideal.

$$q = nC\Delta T, \Delta T = \frac{q}{nC}$$

$$\text{Linear, } C_v = \frac{5}{2}R = 20.79 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\text{Linear, } C_p = \frac{7}{2}R = 29.10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

(a) At constant volume

$$\Delta T = \frac{q}{nC_v} = \frac{500. \text{ J}}{0.900 \text{ mol} \times 20.79 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} = + 26.7 \text{ K}$$

$$T_{\text{final}} = 298.0 + 26.7 = 324.7 \text{ K}$$

$$\Delta U = q + w, \quad \Delta U = q + 0 = 500. \text{ J}$$

(b) At constant Pressure

$$\Delta T = \frac{q}{nC_p} = \frac{500. \text{ J}}{0.900 \text{ mol} \times 29.10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} = + 19.1 \text{ K}$$

$$T_{\text{final}} = 298.0 + 19.1 = 317.1 \text{ K}$$

To find out the change of internal energy - design a two steps procedure.

- 1) Increase temperature in constant volume (C_v): $w = 0$, $\Delta U_1 = q$
 $= 0.900 \text{ mol} \times 20.79 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 19.1 \text{ K} = 357 \text{ J}.$
- 2) isothermal expansion to 1 atm, $\Delta U_2 = 0.$

Since U is state function, total $\Delta U = + 357 \text{ J}.$

At constant volume, no work, all heat is converted to internal energy, temperature is higher. At constant pressure, there is a work, fewer energy is converted to internal energy, temperature is lower.

The Enthalpy of Physical Change

Vaporization, requires adding energy to break and separate intermolecular attractions, is an endothermic process.

Freezing, is exothermic because energy is given off to allow stronger intermolecular attractions to form between molecules.

Phase changes usually take place at constant pressure, the heat transfer is due to changes in enthalpy.

Enthalpy of vaporization

Liquid to a gas or vaporizing is called the enthalpy of vaporization:

$$\Delta H_{\text{vap}} = H_{\text{m}}(\text{vapor}) - H_{\text{m}}(\text{liquid})$$

Where ΔH_{m} is the molar heat

For water at its boiling point, 100°C, $\Delta H_{\text{vap}} = 40.7 \text{ kJ}\cdot\text{mol}^{-1}$, and at 25°C the value is $\Delta H_{\text{vap}} = 44.0 \text{ kJ}\cdot\text{mol}^{-1}$.

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

Enthalpy of fusion

Solid to a liquid or melting (fusion) is called the enthalpy of fusion,

$$\Delta H_{\text{fus}} = H_{\text{m}}(\text{liquid}) - H_{\text{m}}(\text{solid})$$

The enthalpy of fusion of water at 0.0 °C is 6.0 kJ·mol⁻¹: to melt 1.0 mol H₂O(s) (18 g of ice) at 0.0 °C, we have to supply 6.0 kJ of heat.

This is much less than the enthalpy of vaporization (more than 40 kJ) where molecules are separated completely. In **melting**, the molecules stay close together, and the intermolecular forces change is small.

All enthalpies are positive. Stronger intermolecular forces, such as hydrogen bonds*, have the highest enthalpies of vaporization.

		Freezing/Boiling Points (K)	$\Delta H_{\text{fus}}^{\circ}/\Delta H_{\text{vap}}^{\circ}$
Argon	Ar	83.8/87.3	1.2/6.5
Methane	CH ₄	90.7/112	0.94/8.2
Acetone	CH ₃ COCH ₃	178/329	5.72/29.1
Methanol*	CH ₃ OH	175/338	3.16/35.3
Ammonia*	NH ₃	195/240	5.65/23.4
Water*	H ₂ O	273/373	6.01/40.7

Enthalpy of freezing

Freezing is the change from liquid to solid.

Enthalpy of fusion = - Enthalpy of freezing

Enthalpy of condensation

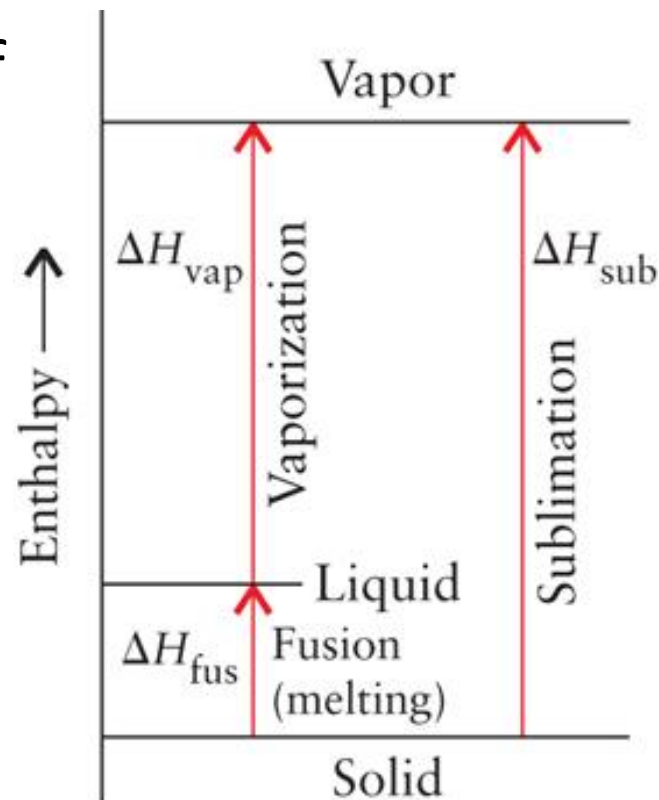
Condensation is the change from gas to liquid. So

$$\Delta H_{\text{condensation}} = - \Delta H_{\text{vap}}.$$

Enthalpy Sublimation

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

$$\Delta H_{\text{sublimation}} = H_m(\text{vapor}) - H_m(\text{solid})$$



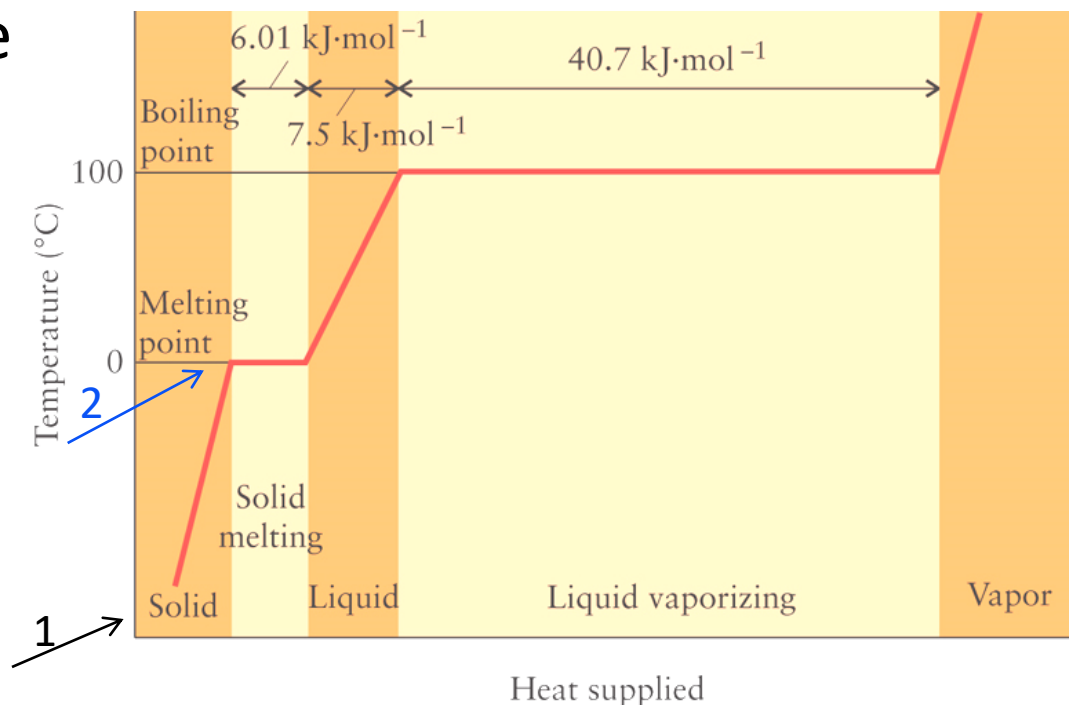
Deposition

Deposition is the reverse of sublimation a vapor into its solid. $\Delta H_{\text{deposition}} = H_m(\text{solid}) - H_m(\text{vapor}) = -\Delta H_{\text{sublimation}}$

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.

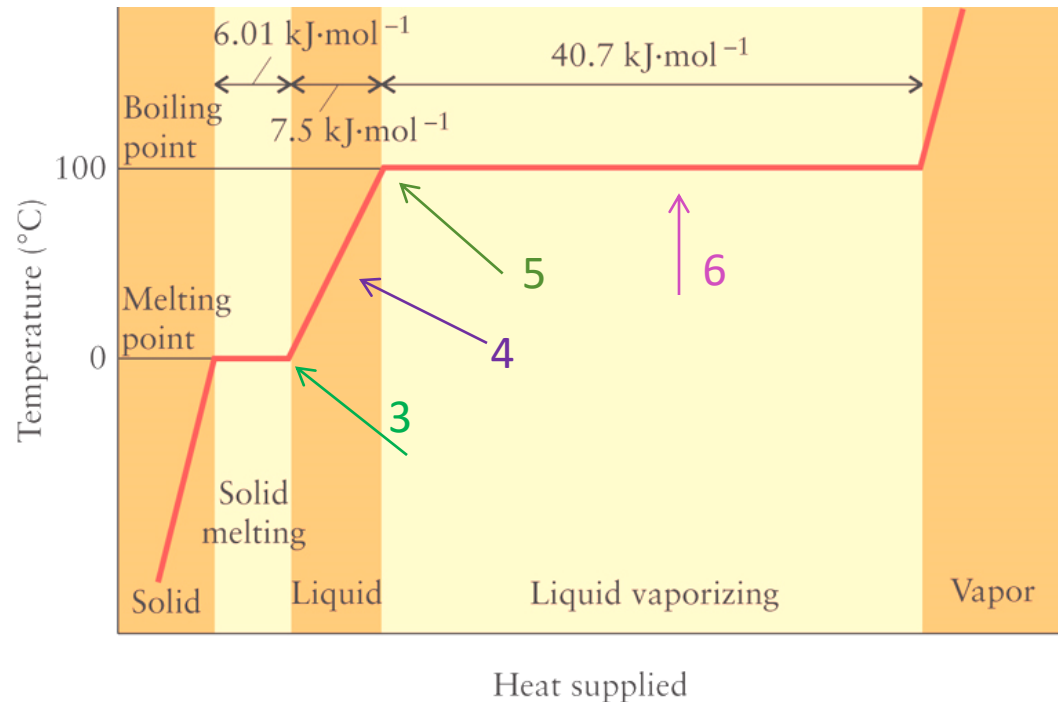


1. In a solid the molecules are still locked together, as they oscillate vigorously around their mean positions.

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.

Heating Curves

3. At this temperature, all the added energy is used break all the attractive forces, the temperature remains constant at the melting point until all the ice has melted.



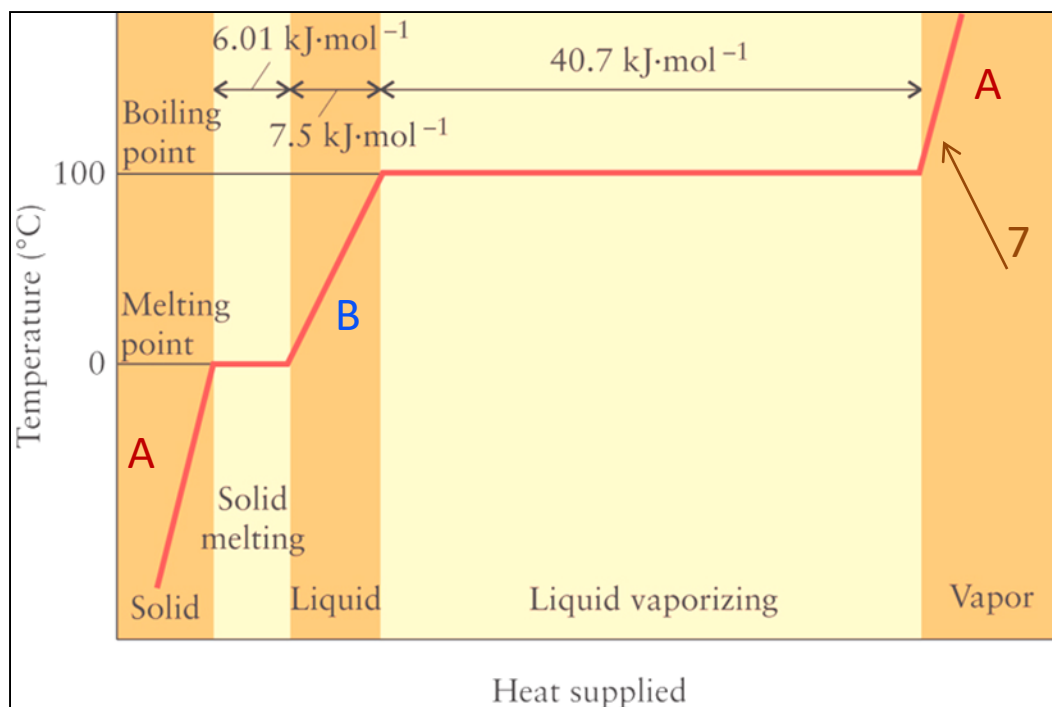
4. Only then does the temperature rise again, and the rise continues right up to the boiling point.

5. At the boiling point, the temperature rise again comes to a halt.

6. Now the water molecules have enough energy to escape into the vapor state, and all the heat supplied is used to form the vapor.

Heating Curves

7. After the sample has evaporated and heating continues, the temperature of the vapor rises again.



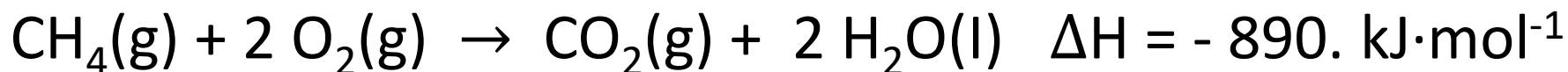
A. Steeper slopes mean lower the heat capacity. Both the solid and vapor phases have steeper slopes so the liquid (**B**) has a greater heat capacity.

B. The differences in heat capacity are because: In liquid, the energy goes to large variation of **intermolecular** bonds. In solid the energy goes to atoms **vibrations** on lattices, and in gas the energy mostly goes to **individual** molecules.

Enthalpy of Chemical Change

Every chemical reaction is accompanied by energy transfer as heat.

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



The stoichiometric coefficients corresponding to the quantity involved in the enthalpy change.

The Relation Between ΔH and ΔU

- If no gas is generated or consumed in a reaction, little expansion work is done the difference between ΔH and ΔU is negligible; so we have

$$\Delta H = \Delta U$$

- 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 calculate $P\Delta V$:

$$\Delta H = \Delta U + \Delta nRT$$

Example 8.8 A constant-volume calorimeter showed that the heat generated by the combustion of 1.000 mol glucose molecules in the reaction $\text{C}_6\text{H}_{12}\text{O}_6(\text{g}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$ is 2559 kJ at 298K, and so $\Delta U = -2559 \text{ kJ}$. What is the change in enthalpy for the same reaction?

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

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

$$R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\begin{aligned}\Delta H &= -2559 \text{ kJ} + (6 \text{ mol} \times 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 298 \text{ K}) \\ &= -2559 \text{ kJ} + 14.9 \text{ kJ} = -2544 \text{ kJ}\end{aligned}$$

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.

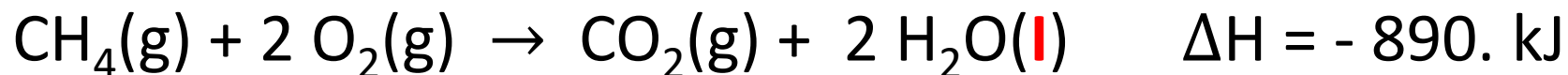
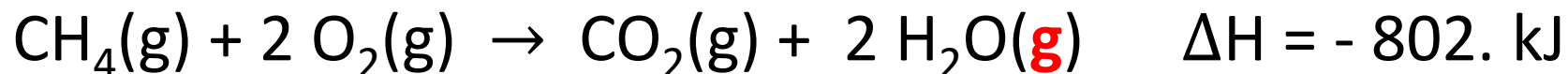
Standard Reaction Enthalpies

Standard State:

- Matter in its pure form at exactly 1 bar;
- A solution concentration is 1 mol/L;
- Temperature is not in the definition, commonly used is 298.15K.
- The standard value of a property X (that is, the value of X for the standard state of the substance) is denoted X° .

Standard Reaction Enthalpies

Always specify the state of each substance, for methane,



The standard reaction enthalpy, ΔH° , is the reaction enthalpy when reactants are in their standard states.

For a $\Delta H^\circ = -890. \text{ kJ}$ signifies the heat output is 890. kJ when 1 mol $\text{CH}_4(\text{g})$ as pure methane gas at 1 bar is allowed to react with pure oxygen gas at 1 bar to produce products in their standard state.

Combining Reaction Enthalpies: Hess's Law

Enthalpy is a state function

Hess's law: the overall reaction enthalpy is the sum of the reaction enthalpies of the steps into which the reaction can be divided.

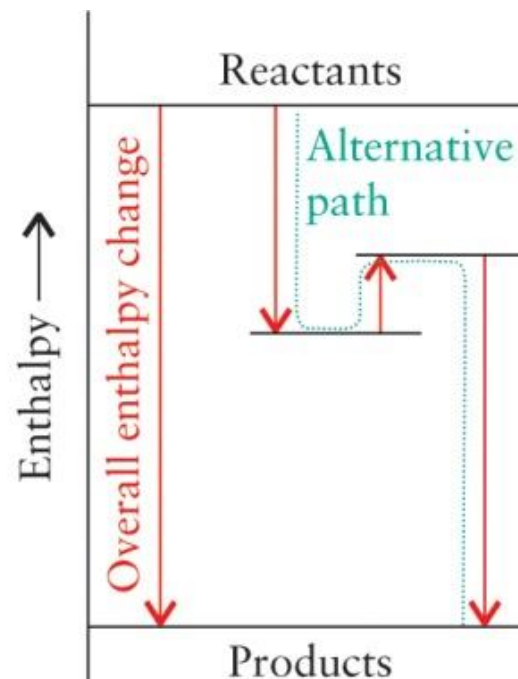


FIGURE 8.30 If an overall reaction can be broken down into a series of steps, then the corresponding overall reaction enthalpy is the sum of the reaction enthalpies of those steps. None of the steps need be a reaction that can actually be carried out.

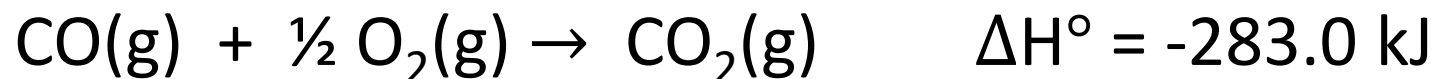
The oxidation of carbon as graphite, denoted C(gr), to carbon dioxide: $\text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

This can be thought of as two different steps.

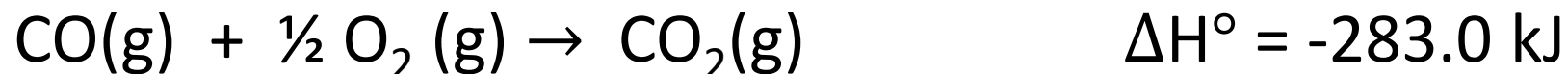
One step is the oxidation of carbon to carbon monoxide:



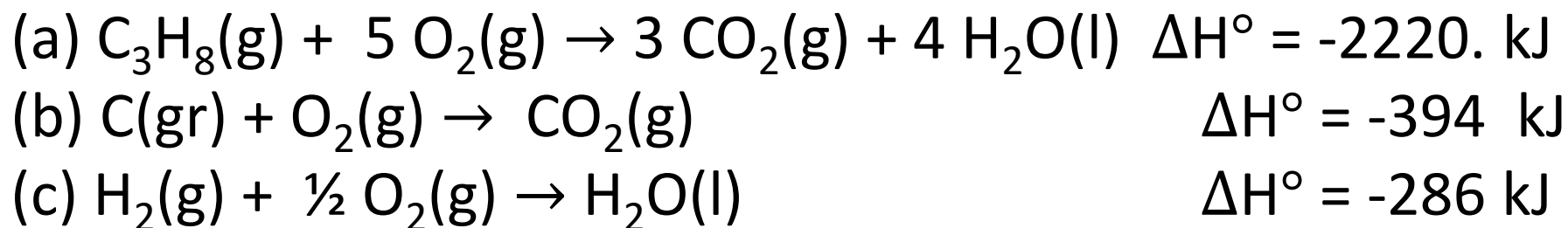
The second step is the oxidation of CO to CO_2 :



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



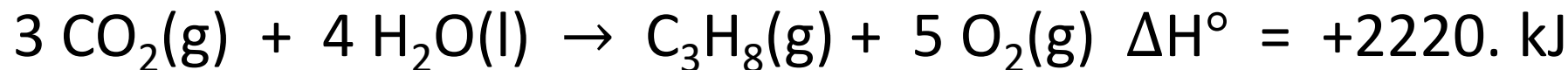
Example 8.9 Using Hess's law, calculate the standard enthalpy for $3 \text{ C}(\text{gr}) + 4 \text{ H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$ from the following experimental data:



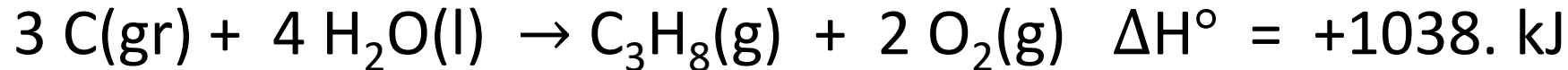
Step 1 Treat carbon as a reactant, (b) and multiply it through by 3.



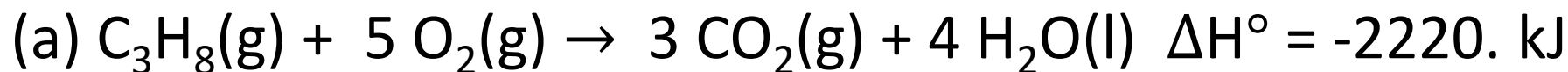
Step 2 Reverse equation (a), changing the sign of H.



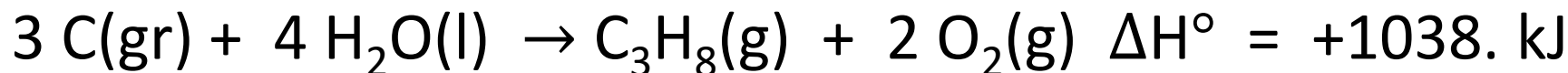
Simplify by combining the two previous equations.



Continued: Overall reaction **$3 \text{ C(gr)} + 4 \text{ H}_2\text{(g)} \rightarrow \text{C}_3\text{H}_8\text{(g)}$**



Previous



Step 3 To cancel unwanted H_2O and O_2 , multiply equation (c) by 4.



Step 4 Combine and simplify



Standard Enthalpies of Formation

It is impractical to list every standard reaction enthalpy.

Using Hess Law:

- Tabulate the "standard enthalpies of formation" of substances.
- Combination of these quantities to obtain the standard enthalpy of reaction needed.

Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			Organic compounds		
ammonia	$\text{NH}_3(\text{g})$	-46.11	benzene	$\text{C}_6\text{H}_6(\text{l})$	+49.0
carbon dioxide	$\text{CO}_2(\text{g})$	-393.51	ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.69
carbon monoxide	$\text{CO}(\text{g})$	-110.53	ethyne	$\text{C}_2\text{H}_2(\text{g})$	+226.73
dinitrogen tetroxide	$\text{N}_2\text{O}_4(\text{g})$	+9.16	(acetylene)		
hydrogen chloride	$\text{HCl}(\text{g})$	-92.31	glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1268
hydrogen fluoride	$\text{HF}(\text{g})$	-271.1	methane	$\text{CH}_4(\text{g})$	-74.81
nitrogen dioxide	$\text{NO}_2(\text{g})$	+33.18			
nitric oxide	$\text{NO}(\text{g})$	+90.25			

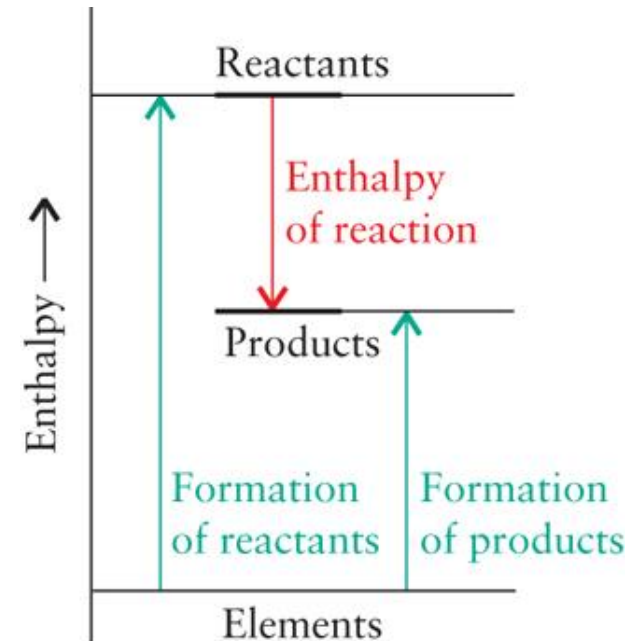


Combining standard enthalpies of formation to calculate a standard reaction enthalpy.

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.



$$\Delta H^{\circ} = \sum n \Delta H_f^{\circ} (\text{products}) - \sum n \Delta H_f^{\circ} (\text{reactants})$$

n is the amounts in moles, Σ (sigma) means sum.

The Born-Haber Cycle

In Section 2.4 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.

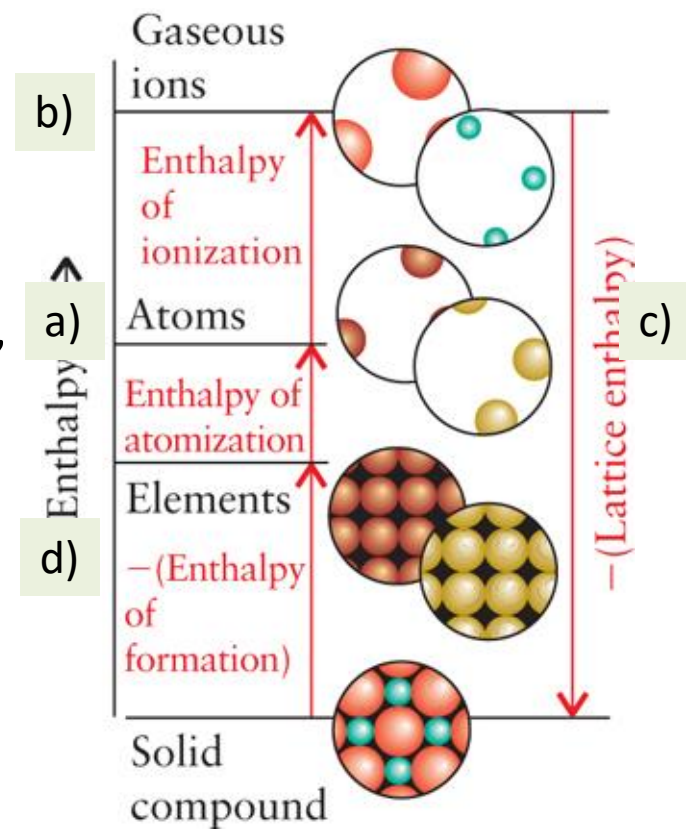
Instead we measure it indirectly by using an application of Hess's law.

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

The Born-Haber Cycle

The **Born-Haber cycle** is a closed path of steps.

- a) break apart the bulk elements into atoms,
- b) ionize the atoms,
- c) combine the gaseous ions to form the ionic solid,
- d) then form the elements again from the ionic solid,



The sum of a complete Born-Haber cycle is **zero**, because the enthalpy of the system must be the same at the **start and finish**.

Note: Lattice energies are “-”, though when calculated with the Born-Haber cycle the value will be positive.

The Reaction Enthalpy from Bond Enthalpies

In chemical reactions, old bonds break and new ones form. We can estimate reaction enthalpies if we know the enthalpy changes associated with bond breaking for formation.

TABLE 7.8 Mean Bond Enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$)

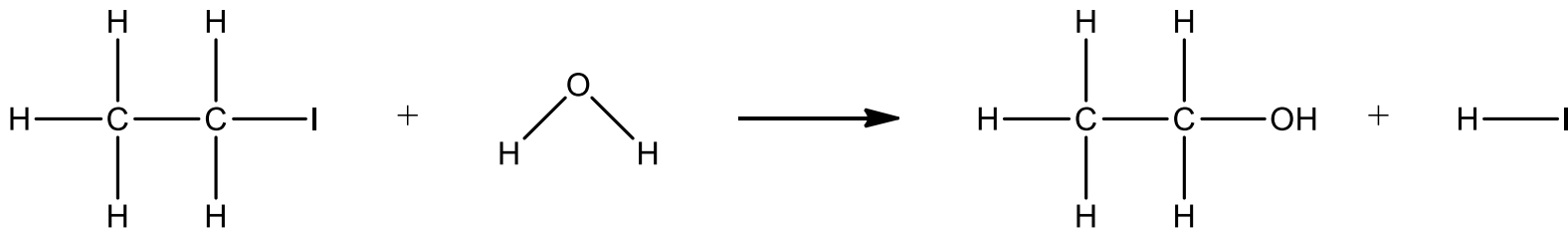
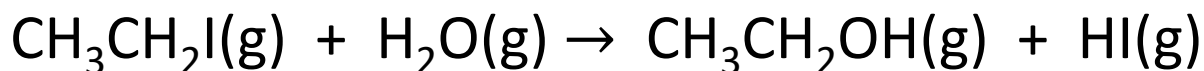
Bond	Mean bond enthalpy	Bond	Mean bond enthalpy
C—H	412	C—I	238
C—C	348	N—H	388
C=C	612	N—N	163
C \cdots C*	518	N=N	409
C \equiv C	837	N—O	210.
C—O	360	N=O	630.
C=O	743	N—F	195
C—N	305	N—Cl	381
C—F	484	O—H	463
C—Cl	338	O—O	157
C—Br	276		

*In benzene.

The Reaction Enthalpy from Bond Enthalpies

Note that bond breaking is always endothermic and bond formation is always exothermic.

$$\Delta H^\circ = \sum \text{Breaking Bond Enthalpy} - \sum \text{Forming Bond Enthalpy}$$



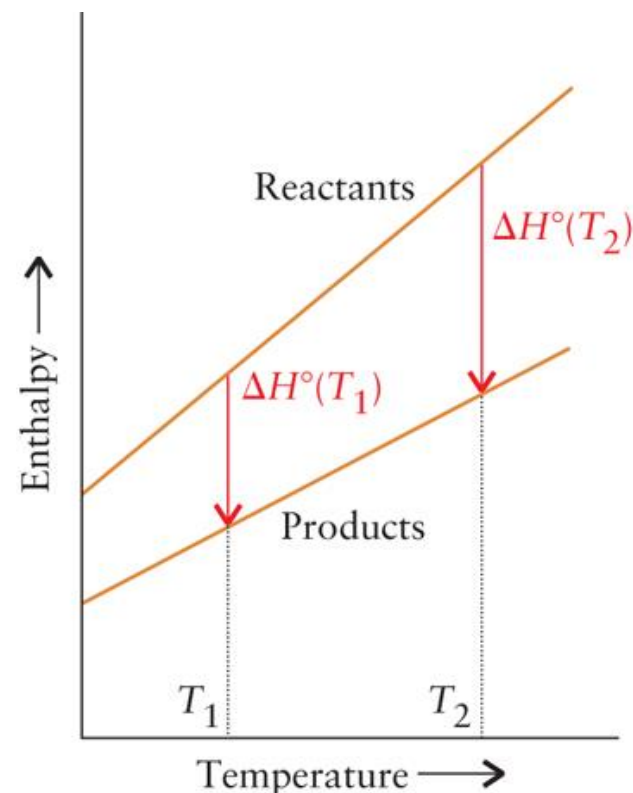
Breaking: C-I 238 kJ·mol⁻¹, O-H 463 kJ·mol⁻¹, Total Breaking = + 701 kJ

Forming: C-O 360 kJ·mol⁻¹, H-I 299 kJ·mol⁻¹, Total Forming = -659 kJ

$$\Delta H^\circ = 701 \text{ kJ} - 659 \text{ kJ} = 42 \text{ kJ}\cdot\text{mol}^{-1}, \quad \text{Endothermic}$$

The Variation of Reaction Enthalpy with Temperature

- How to calculate the reaction enthalpy at different temperatures?
- The enthalpies of both reactants and products increase with temperature.
- The increase in enthalpy depends on its molar heat capacity at constant pressure



$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + (T_2 - T_1) \Delta C_p$$

$$\Delta C_p = \sum n C_{p,m}(P) - \sum n C_{p,m}(R)$$