

화학 General Chemistry

034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

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Thermodynamics

Thermodynamics: transformation and transfer of energy

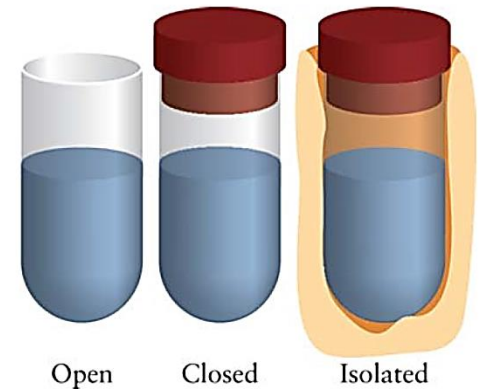
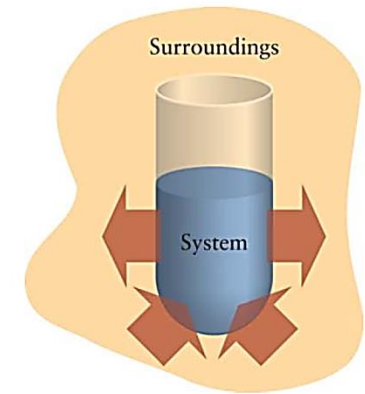
: two ways in which energy can be transferred.

- Predicts the “**direction**” of chemical and physical changes at a given temperature.
Ex) $\text{H}_2\text{O} (s) \rightarrow \text{H}_2\text{O} (l)$ at room temp?
- What is the most stable state of matter?

Systems, States, and Energy

7.1. Systems

- **System**: the region in which we are interested
- **Surroundings**: everything else
- **Universe**: system + surroundings



- **Open system**: exchanging **both matter and energy** with the surroundings
ex) car engines
- **Closed system**: a fixed amount of matter, but exchanging **energy** with the surroundings
ex) ice pack
- **Isolated system**: **no** contact with the surroundings
ex) thermos bottle

7.2. Work and Energy

Force: changes the state of motion of an object (N, $\text{kg} \cdot \text{m} \cdot \text{s}^{-2}$):

Work: the process of moving an object against an opposing force

$$\text{Work} = \text{force} \times \text{distance} \text{ (J, } \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}\text{)}$$

Energy: the capacity of a system to do **work**

Internal Energy (U): the total amount of energy in a system

-Absolute value of U cannot be measured.

Change of the internal energy of a system

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

-Internal energy

= Potential energy

+ Kinetic energy induced by thermal motion of molecules

Work

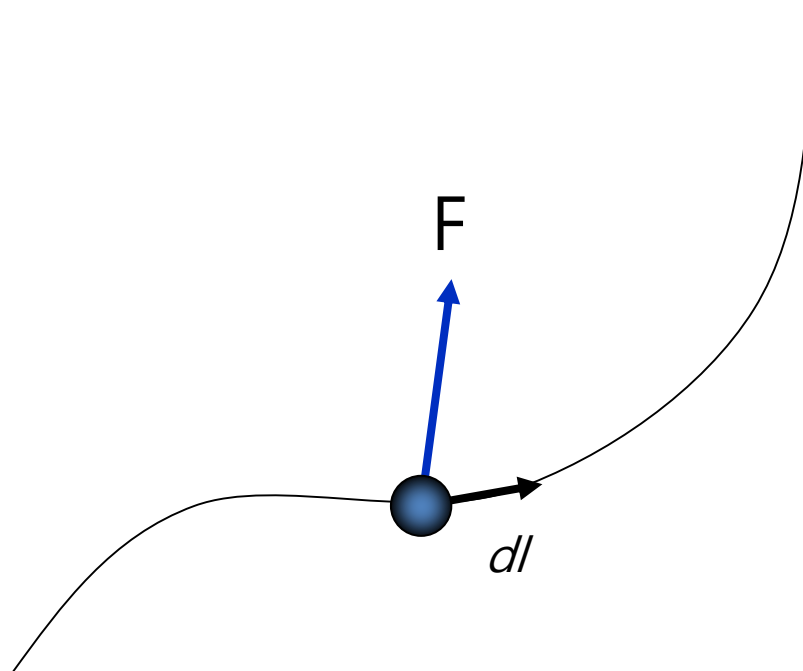
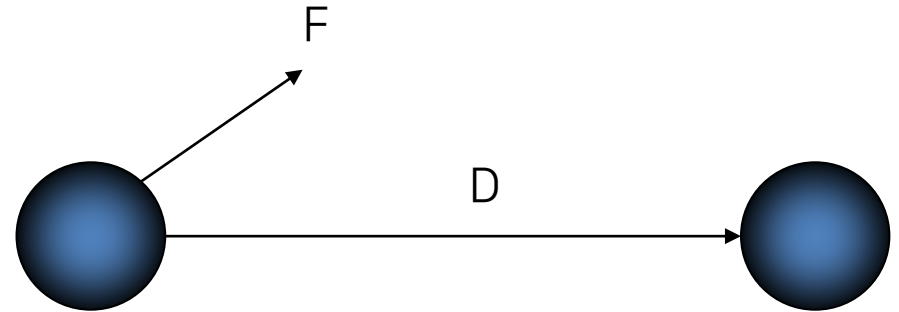
Work = force X distance (J, $\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$)

For constant Force,

$$W = F \cdot D$$

$$W = \int F \cdot dl$$

along a path

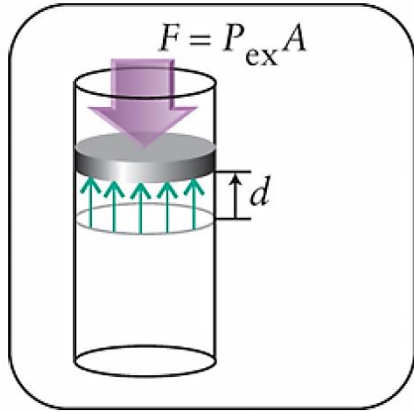


Types of works (w)

Type of work	w	Comment	Units*
expansion	$-P_{\text{ex}}\Delta V$	P_{ex} is the external pressure ΔV is the change in volume	Pa m^3
extension	$f\Delta l$	f is the tension Δl is the change in length	N m
raising a weight	$mg\Delta h$	m is the mass g is the acceleration of free fall Δh is the change in height	kg $\text{m}\cdot\text{s}^{-2}$ m
electrical	$\phi\Delta q$	ϕ is the electrical potential Δq is the change in charge	V C
surface expansion	$\gamma\Delta A$	γ is the surface tension ΔA is the change in area	$\text{N}\cdot\text{m}^{-1}$ m^2

- Expansion work: the work arising from a change in the volume of a system ex) piston/cylinder
- Non-expansion work ex) battery, human body

7.3 Expansion Work



Work = $P_{\text{ex}} A \times d$ Work = force X distance (J, $\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$)

$$A \times d = \Delta V$$

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

w = energy transferred **to** a system by doing work;
negative value!

- Free expansion: $P_{\text{ex}} = 0$ (vacuum) $\rightarrow w = 0$
- Unit: $\text{Pa} \cdot \text{m}^3 = \text{kg} \cdot \text{m} \cdot \text{s}^{-2} \cdot \text{m} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = \text{J}$
- $1\text{L} \cdot 1\text{atm} = 10^{-3} \text{m}^3 \times 101325 \text{Pa} = 101.325 \text{Pa} \cdot \text{m}^3 = 101.325 \text{J}$

$$P = \frac{F}{A}: 4\text{장 참조}$$

$$\begin{aligned} F (\text{N}) &= ma: \text{kg} \times (\text{m}/\text{s}^2) \\ \text{Area: } &\text{m}^2 \\ P &= \text{kg} \times (\text{m}/\text{s}^2) / \text{m}^2 = \text{kg m}^{-1} \text{s}^{-2} \end{aligned}$$

Thermodynamic process: Reversible process vs. Irreversible process

Reversible process: a process whose direction can be "reversed" by inducing infinitesimal changes to some property of the system via its surroundings.

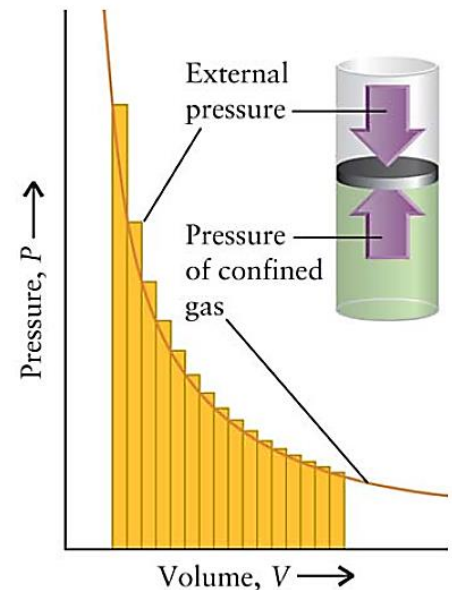
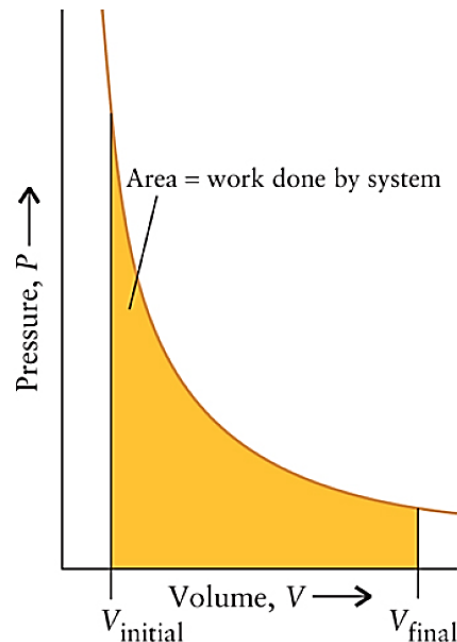
Irreversible processes are a result of straying away from the curve, therefore decreasing the amount of overall work done; an irreversible process can be described as a thermodynamic process that leaves equilibrium

Reversible Process

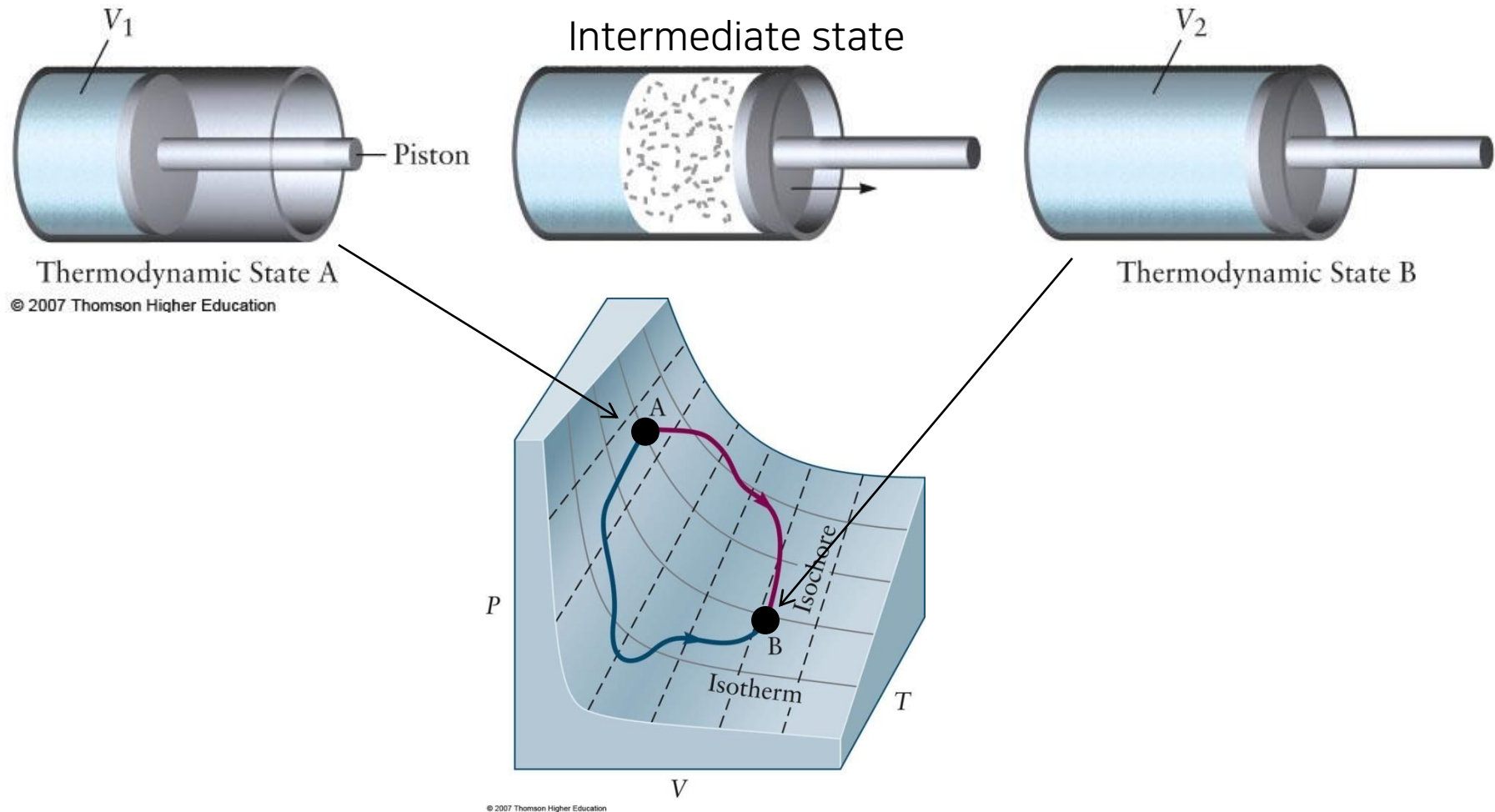
$$dw = -PdV$$

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

$$w = -nRT \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{dV}{V} = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$



Reversible versus irreversible state:



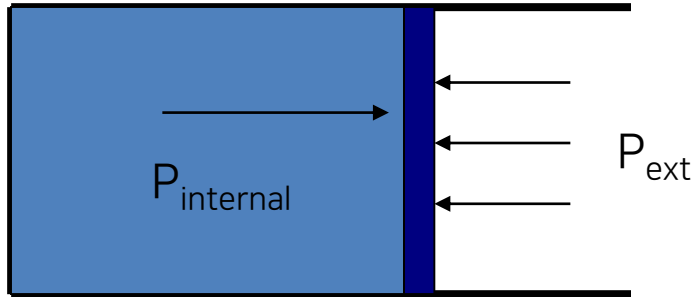
Reversible process:

intermediate state almost remains on the PVT surface

Irreversible process:

intermediate state do **not** stay on the PVT surface.

Reversible vs Irreversible work



$$P_{\text{int}} = P_{\text{ext}}$$

Reversible work

$$P_{\text{int}} \neq P_{\text{ext}}$$

Irreversible work

(Example)

- Ar gas at room temperature is expanded from 1 liter to 10 liter against external pressure of 1 atm. What is the w ?

Expansion : $w < 0$
Compression : $w > 0$

Hydrogen gas is expanded from 0.1 liter to 10 liter *in vacuum*. What is the work done on the gas?

$P_{\text{ext}} = 0$ (No external pressure)

$$w = -P_{\text{ext}} \Delta V = 0$$

Temperature and Heat

Work, Heat: two ways in which energy can be transferred.

- *Temperature:*

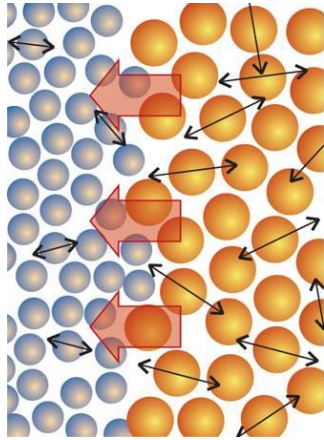
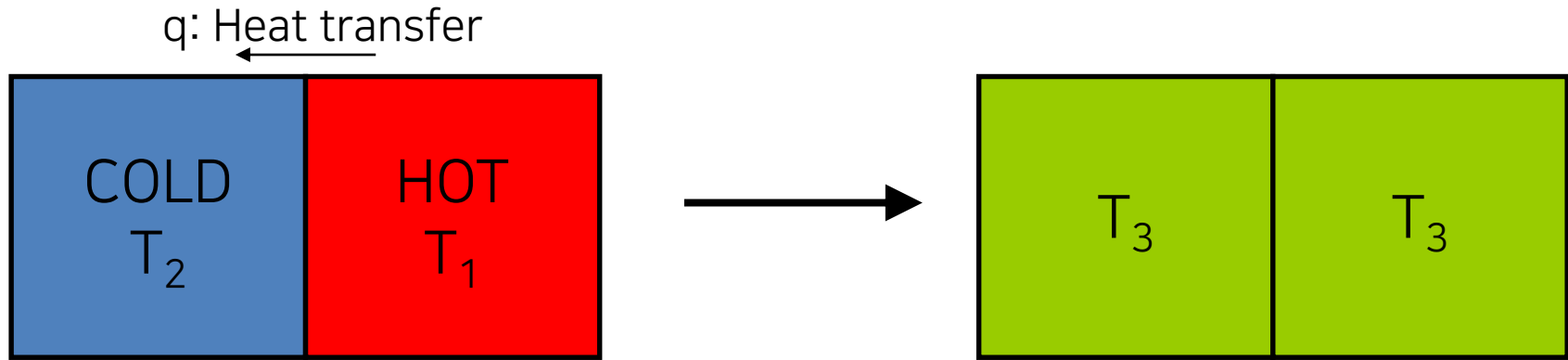
Proportional to the kinetic energy of molecules moving in random directions

For ideal gas, $KE = \frac{3}{2} RT$
(thermal energy)

- *Heat: q*

Transfer of thermal energy from one region to another

Heat (transfer), q : Energy transferred as a result of a temperature difference

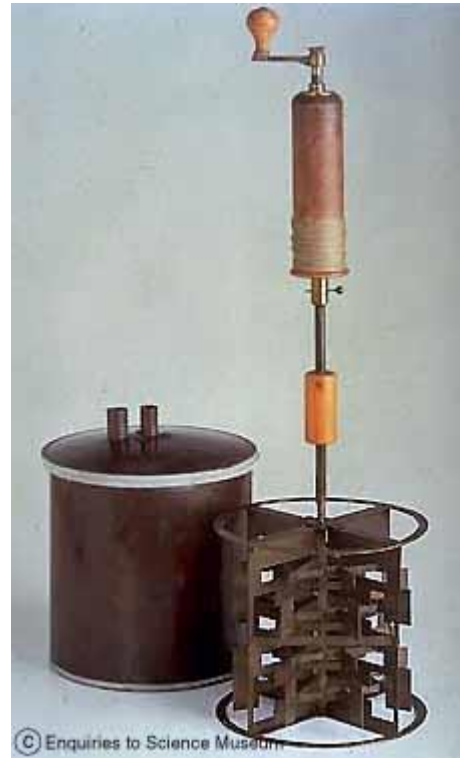
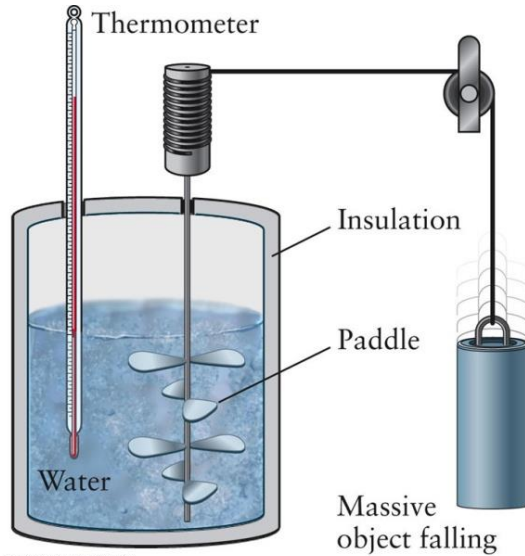


Heat (thermal energy) is transferred from HOT to COLD region until two regions have the same thermal energy

Temperature difference \rightarrow heat transfer
(from hot to cold regions)

- q = *the energy transferred **to** a system as heat*
 - Unit: J , cal ($1\ cal = 4.184\ J$)
- * food calorie = Cal = kcal

Work and heat are the different form of energy



Work: energy associated with overall **directed motion** of molecules.

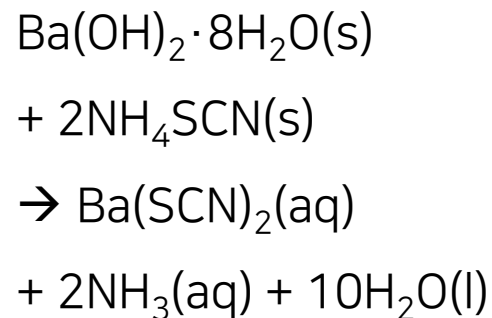
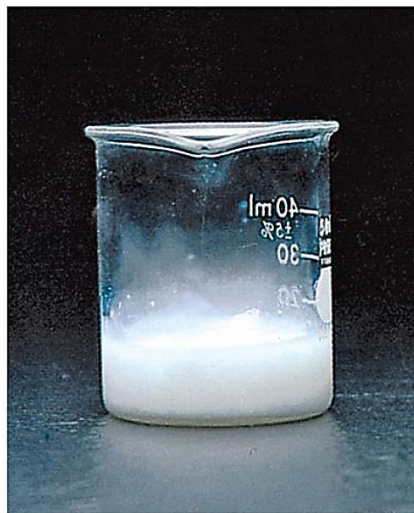
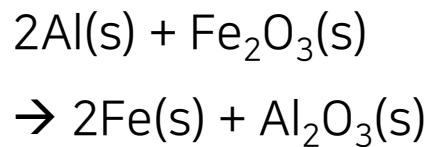
Heat: energy associated with **random motion** of molecules.

<https://www.youtube.com/watch?v=5yOhSIAIPRE>

<https://www.youtube.com/watch?v=MBrTDKc9YZ0>

7.5 The Measurement of Heat

- Exothermic process vs. Endothermic process



- Adiabatic: $q = 0$ (Not an isolated system: $\Delta \text{Internal Energy } (\Delta U) = w$)
- Diathermic: $q \neq 0$
- Heat capacity (C)

$$C = \frac{\text{heat supplied}}{\text{temperature rise produced}} = \frac{q}{\Delta T}$$

- Measurement of heat and heat capacity (calorimeter)

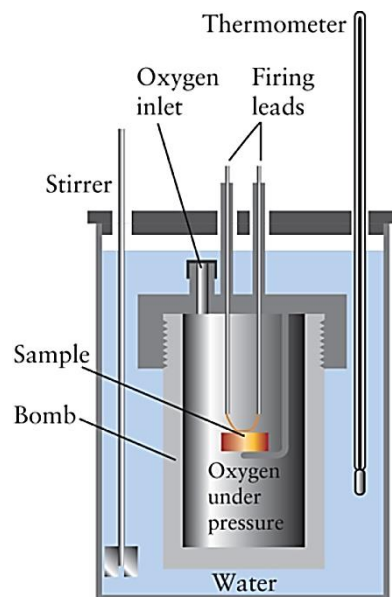
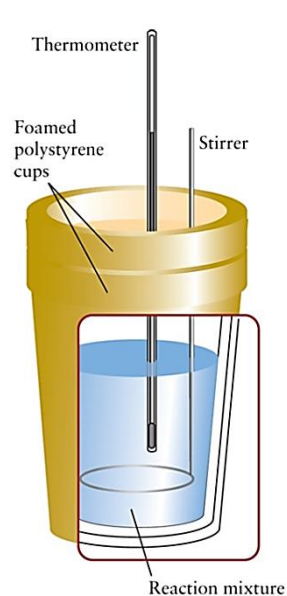


TABLE 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H ₂ O	4.184
C ₂ H ₅ OH (ethanol)	2.46

Material	Specific heat capacity ($\text{J}\cdot(^{\circ}\text{C})^{-1}\cdot\text{g}^{-1}$)	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

Specific heat capacity (C_s) = C/m

Molar heat capacity (C_m) = C/n

$$q = C\Delta T = mC_s\Delta T$$

$$= nC_m\Delta T$$

Calculate the **heat** required to increase 20.0°C from room temperature of
 (a) water 100g, (b) water 2.00 mol

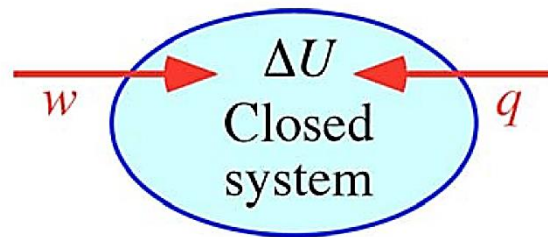
7.6 The 1st Law of Thermodynamics

The 1st law of thermodynamics

$$\Delta U (\Delta E) = q + w$$

where, U = internal energy of a system

It is applicable to any process that begins and ends in equilibrium state

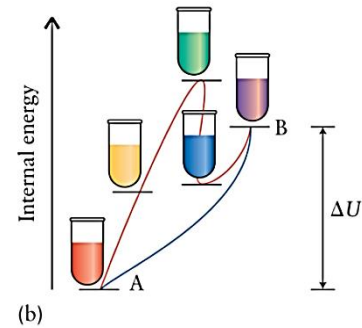
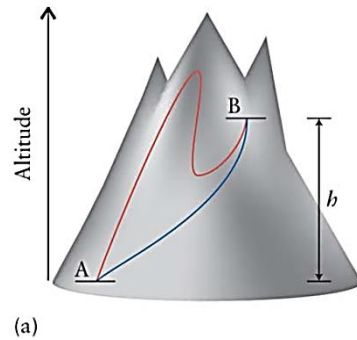


- Other formal states of the 1st law are:

1. Although energy assumes many forms, the total quantity of energy is **constant**, and when energy disappears in one form it appears simultaneously in other forms.
2. All the energies received turned into the energy of the **system**.
3. The total energy of an isolated system is **constant**.

State function vs. Path function

- **State** function: a property that depends only on the **current state** of the system and is **independent** of how the state was prepared.
- **Path** function: a property depends on the **path** taken to reach one state from another.



- Although **q** and **w** are path functions, $\Delta U = q + w$ is a state function.

For the **all ideal gases**, $\Delta U = 0$ for isothermal processes including expansion/compression.

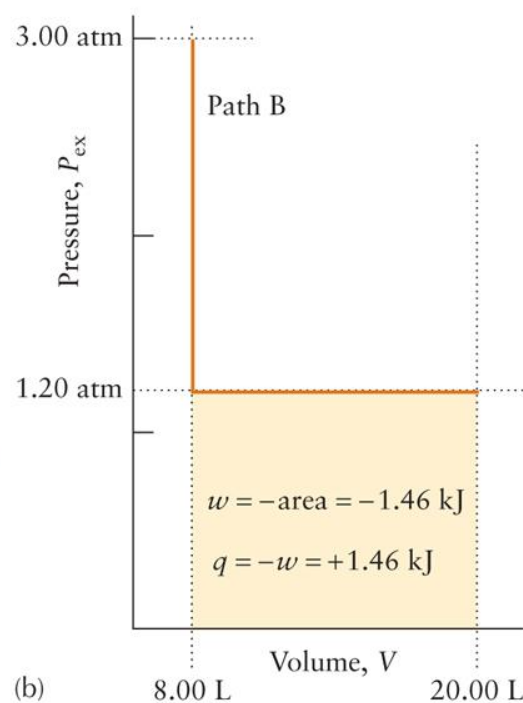
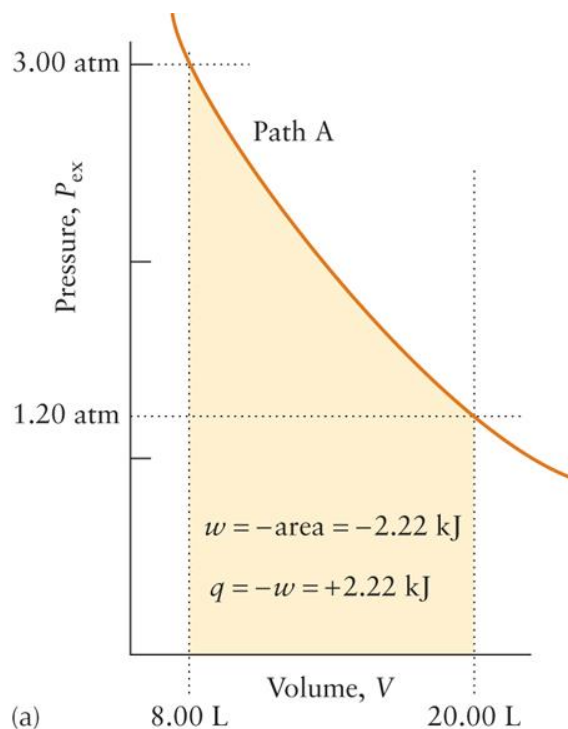
- Move at the same average speed; kinetic energy remains the same.
- No interaction between the molecules: no change in potential energy

For gas expansion,

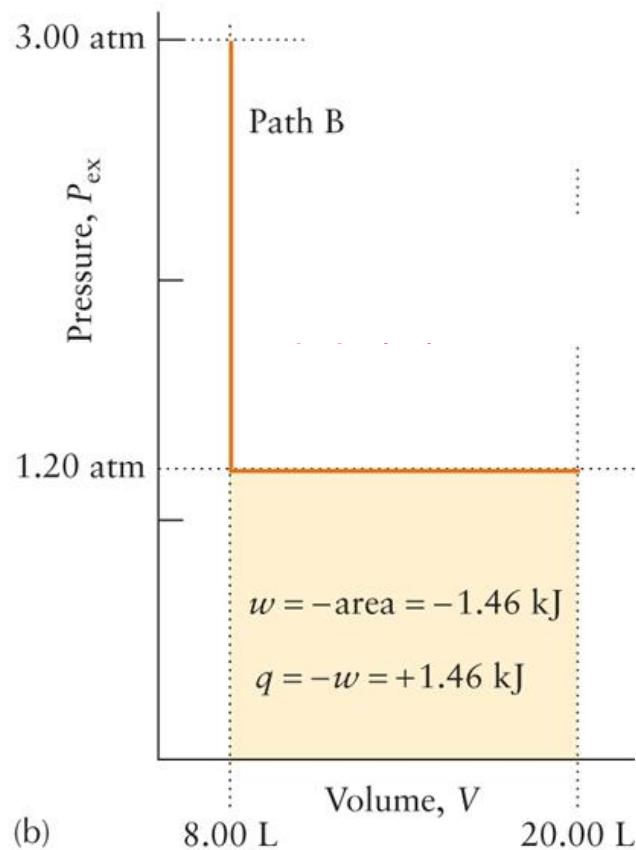
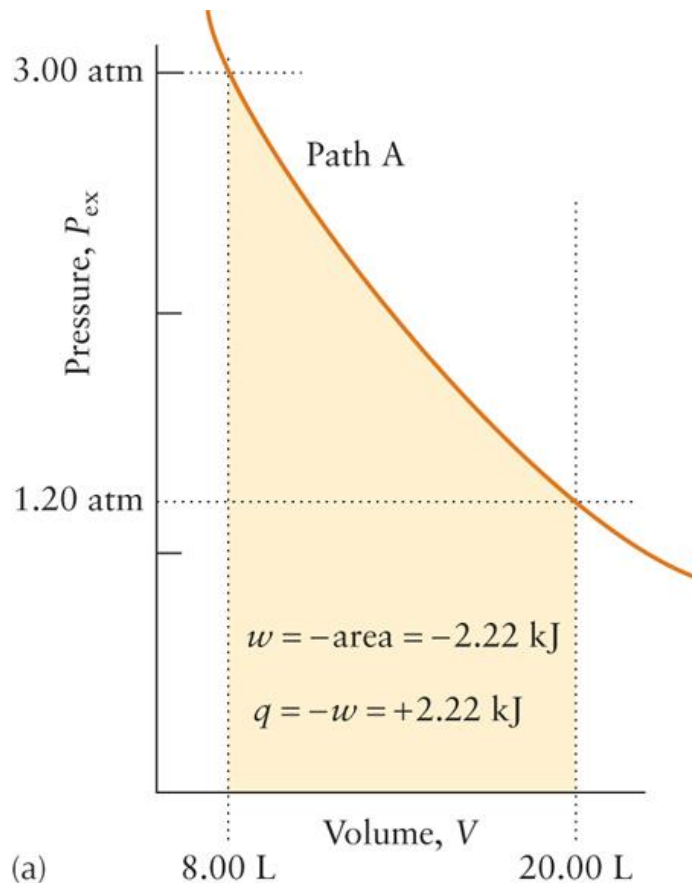
Suppose that **1.00 mol** of **ideal gas** molecules at an initial pressure of **3.00 atm** and **292 K** **expands** against a constant external pressure of **1.20 atm** from **8.00 L** to **20.00 L** by two different paths.

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

(b) Path B, a hypothetical alternative to path A, has two steps: 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. Determine for each path the work done (w), the heat transferred (q), and the change in internal energy (ΔU).



For gas expansion,



$$dw = -PdV$$

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

$$w = -nRT \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{dV}{V} = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$

$$|w_{\text{rev}}| > |w_{\text{irrev}}|$$

$$|\Delta U_{\text{rev}}| = |\Delta U_{\text{irrev}}| = 0$$

$$|q_{\text{rev}}| > |q_{\text{irrev}}|$$

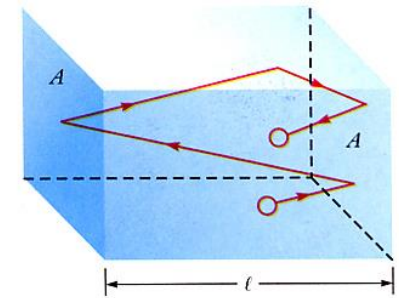
In Chapter 4: The Kinetic Model of Gases

for 1 mol of ideal gas, $\overline{E_k} = \frac{1}{2} M \overline{v^2} = \frac{3}{2} RT$

atomic mass

for each molecule, $\overline{E_k} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$

mass of an atom



$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}$$

- Physical meaning of temperature:

$$T = (2/3R) (\text{KE}):$$

"Temperature is a measure of random kinetic energy"

High-temperature → Molecules move faster

Low-temperature → Molecules move slower

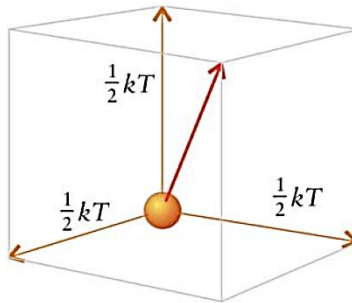
With absolute zero temperature

→ Molecules do not move at all.

7.7 A Molecular Interlude: The Origin of Internal Energy (= kinetic energy)

Equipartition theorem*

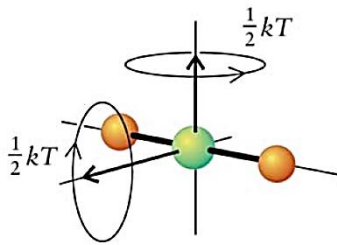
k_B : Boltzmann's constant
 R : gas constant
 N_A : Avogadro's constant



(a)

Monatomic ideal gas (translational motion)

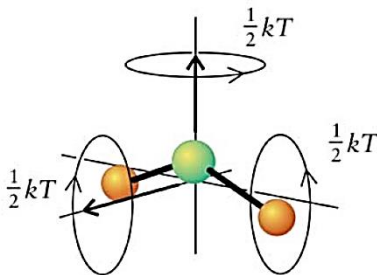
$$U = \frac{3}{2} k_B T \times N_A = \frac{3}{2} RT$$



(b)

Linear ideal gas (translational + rotational)

$$U = \left(\frac{3}{2} k_B T + \frac{2}{2} k_B T \right) \times N_A = \frac{5}{2} RT$$



(c)

Nonlinear ideal gas (translational + rotational)

$$U = \left(\frac{3}{2} k_B T + \frac{3}{2} k_B T \right) \times N_A = 3RT$$

Q. Estimate the contribution of motion to the molar **internal energy** of (a) water vapor (b) acetylene (HCCH, C_2H_2) (c) Ar at 25 °C

- water: nonlinear molecule

- acetylene: linear molecule

- Ar: monatomic gas

Enthalpy

7.8. Heat Transfers at Constant Pressure

- For **isochoric** process (**constant volume**), if no work other than PV work (=non-expansion work) is done,

equal

space

$$w = \int P dV = 0$$

$$\therefore \Delta U = q + w = q$$

- For **isobaric** process (**constant pressure**), if no work other than PV work is done,

equal

pressure

$$\Delta U = q + w = q - P\Delta V$$

$$\therefore q = \Delta U + P\Delta V = \Delta(U + PV)$$

Most of chemical reactions that we are interested in occur at **1 atm** (constant pressure).

For example,

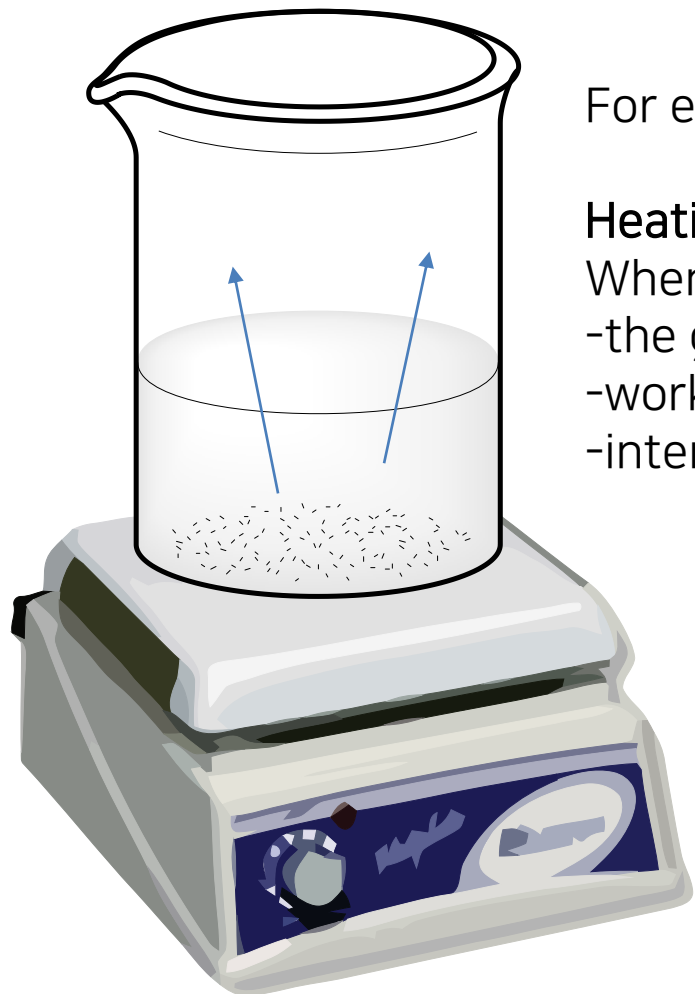
Heating: Heat transfer to the system (q)

When gas is generated,

-the gas pushes the air above the liquid

-work by expansion (even without the piston): $w < 0$

-internal energy: $\Delta U = q + w$



We need a new state function!

- Enthalpy

$$q = \Delta U + P\Delta V = \Delta(U + PV)$$

Most chemical reactions are done under **constant (usually 1 atm) pressure**.
We define another state function, H, enthalpy:

$$H = U + PV$$

Physical meaning of enthalpy:

If

the work done is entirely PV-work (expansion) ,
the external pressure is constant (isobaric),
mechanical equilibrium with internal pressure,

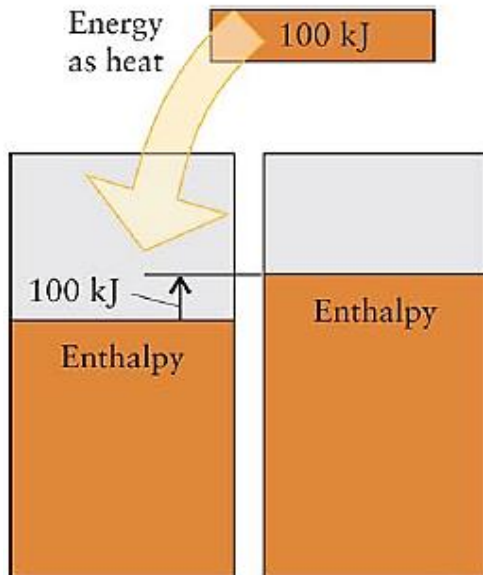
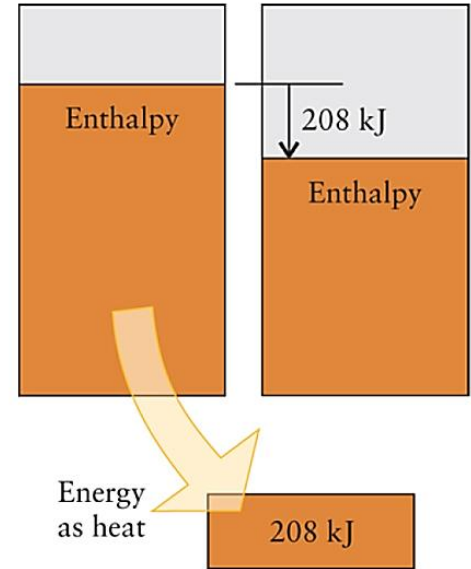
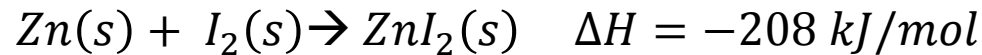
$$\begin{aligned}\Delta H &= \Delta(U + PV) = \Delta U + \Delta(PV) \\ &= \Delta U + \Delta PV + P\Delta V \\ &= (q_p - P_{ext}\Delta V) + 0 + P\Delta V \\ &= +q_p + (P - P_{ext})\Delta V = +q_p\end{aligned}$$

$$q_p = \Delta H = nC_p\Delta T$$

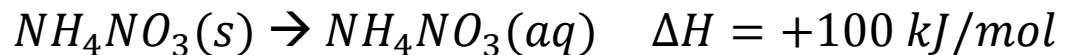
* The enthalpy change
under constant p is the q_p

- Most chemical reactions take place at a **constant pressure** at about 1 atm.

Exothermic reaction ($\Delta H < 0$)



Endothermic reaction ($\Delta H > 0$)



$$q_p = \Delta H = nC_p\Delta T$$

7.9. Heat Capacities at const V and const P

Heat Capacity $C \equiv \frac{q}{\Delta T}$

Heat Capacity at constant V $C_V = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T} \right)_V$ $\Delta U = q + w = q$

Heat capacity at constant P $C_P = \frac{\Delta H}{\Delta T} = \left(\frac{\partial H}{\partial T} \right)_P$ $\Delta H = q$

C_P vs C_V for *ideal gases*

$$C_P = \frac{\Delta H}{\Delta T} = \frac{\Delta (U + PV)}{\Delta T} = \frac{\Delta (U + nRT)}{\Delta T} = C_V + nR$$

$$\therefore C_{P,m} = C_{V,m} + R$$

At constant pressure, not all the heat supplied is used to raise the temperature: some returns to the surroundings as expansion work. In contrast, at constant volume, all the heat energy is used to increase the temperature of the system: lower heat capacity!

7.10. A Molecular Interlude: The Origin of the Heat Capacities of Gases

	Atoms	Linear molecules	Nonlinear molecules
$C_{V,m}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{P,m}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

Example

Calculate the final temperature and the change in internal energy 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

1) O_2 : atoms? **Linear molecules?** Nonlinear molecules?

$$2) C_V = \frac{\Delta U}{\Delta T} = 5/2R = 20.79 \text{ J K}^{-1} \text{ mol}^{-1} \quad C_P = \frac{\Delta H}{\Delta T} = 7/2R = 29.10 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$3) C = \frac{q}{\Delta T}; \Delta T = \frac{q}{C}$$

7.11. The Enthalpy of Physical Change

7.12. Heating Curves

Enthalpy of vaporization

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

Enthalpy of fusion

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

Enthalpy of sublimation

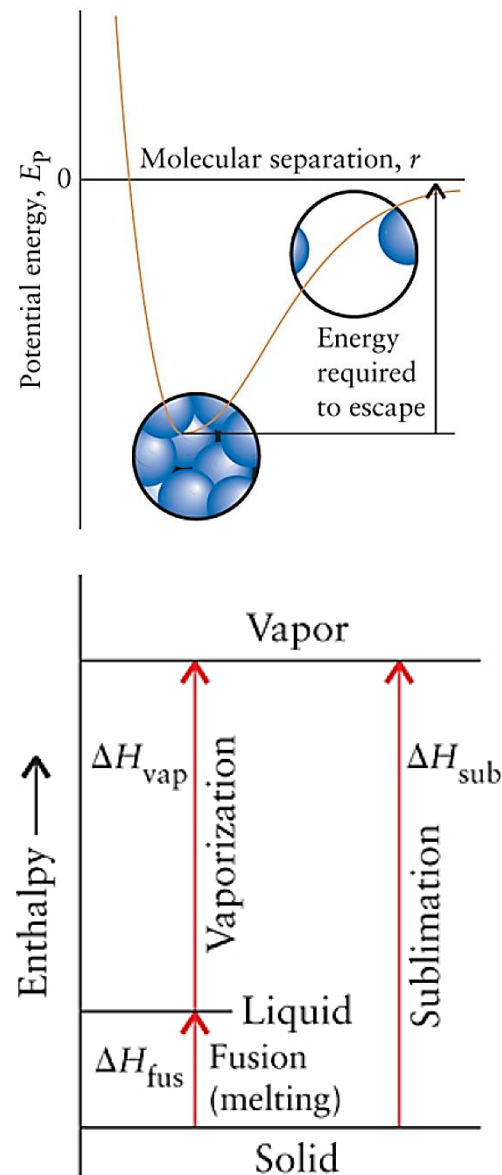
$$\Delta H_{sub} = H(vapor) - H(solid)$$

State function

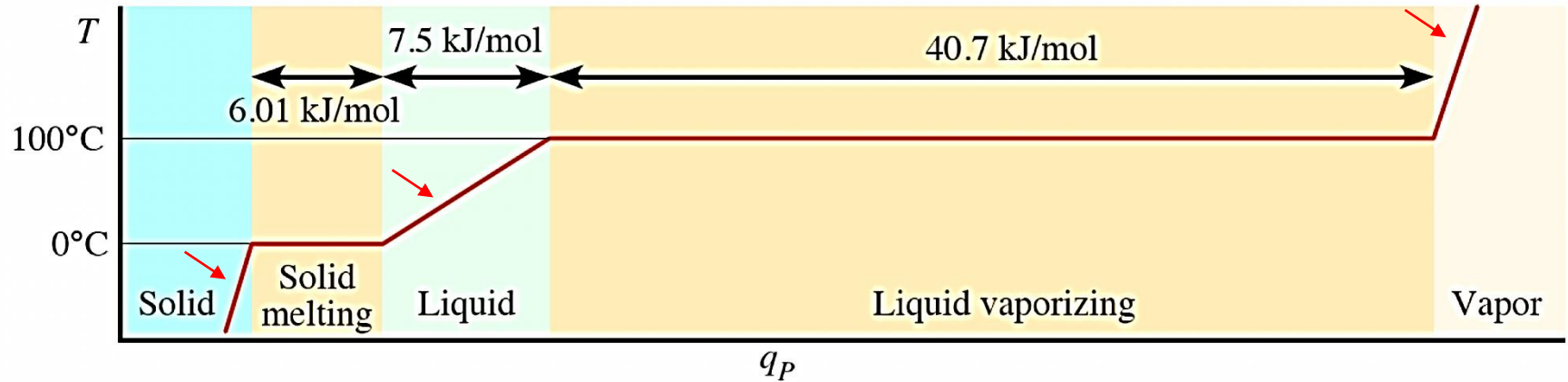
$$\Delta H_{reverse\ process} = -\Delta H_{forward\ process}$$

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

Usually at constant pressure:
heat transfer
= change in enthalpy



Heating Curve (constant P, heating at constant velocity)

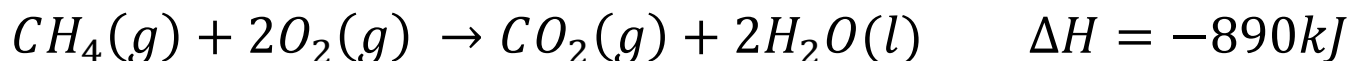
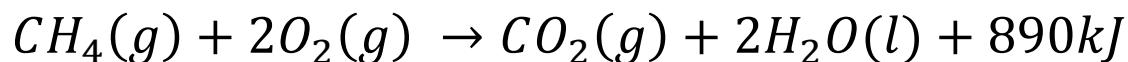


1. The slope \rightarrow heat capacity
2. No temp change during melting/vaporizing

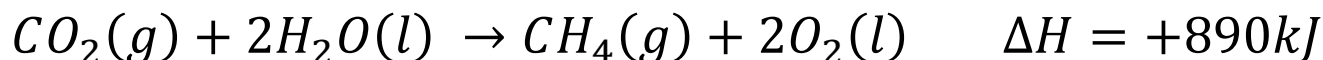
Enthalpy of Chemical Change

7.13. Reaction Enthalpies

Thermochemical equation



Reverse reaction



For reactions in liquids and solids only, $\Delta H \approx \Delta U$ (almost no expansion)

For reactions in which gases are generated, $H = U + PV$

$$\Delta H = H_f - H_i = \Delta U + \underline{(n_f - n_i)RT}$$

Some of the energy is
used for expansion
when $n_f - n_i > 0$.

The difference between H and U. How do they differ in numbers?

Solids:

$\text{CaCO}_3(\text{calcite}) \rightarrow \text{CaCO}_3(\text{aragonite})$

$\Delta U_m = +0.21 \text{ kJ/mole}$, density of calcite = 2.71 g/mL, density of aragonite = 2.93 g/mL,

$$\begin{aligned}\Delta H_m &= \Delta(U_m + PV) = \Delta U_m + \Delta(PV) \\ &= \Delta U_m + P\Delta V_m = \Delta U_m + P(V_m(c) - V_m(a))\end{aligned}$$

$V_m(c)$ = molar volume of calcite = (molar mass of calcite) / density of calcite

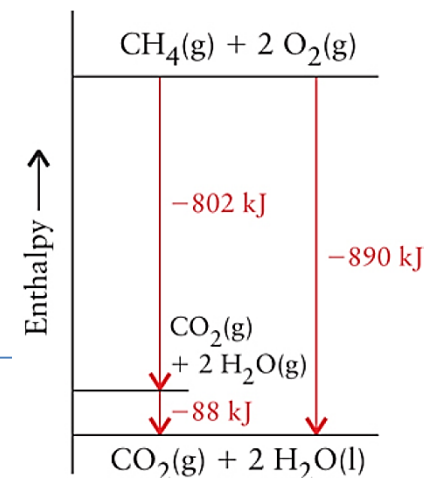
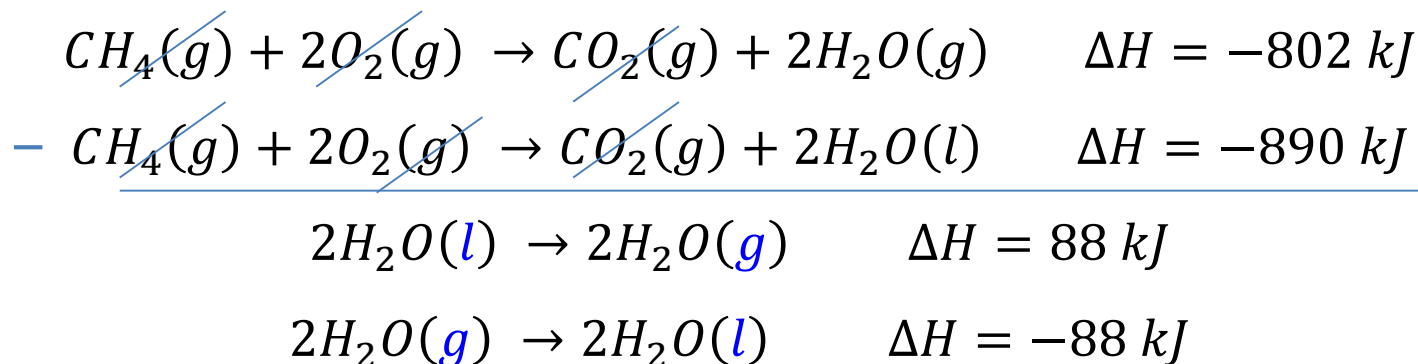
$V_m(a)$ = molar volume of aragonite = (molar mass of aragonite) / density of aragonite

$$\Delta H_m = \Delta(U_m + PV) = \Delta U_m + \Delta(PV) = 0.21 \text{ kJ / mole} + (-0.3 \text{ J / mole}) \cong 0.21 \text{ kJ / mole}$$

U and H are almost the same for solids !!!!

7.14. Standard Reaction Enthalpies

Physical states of the reactants and products



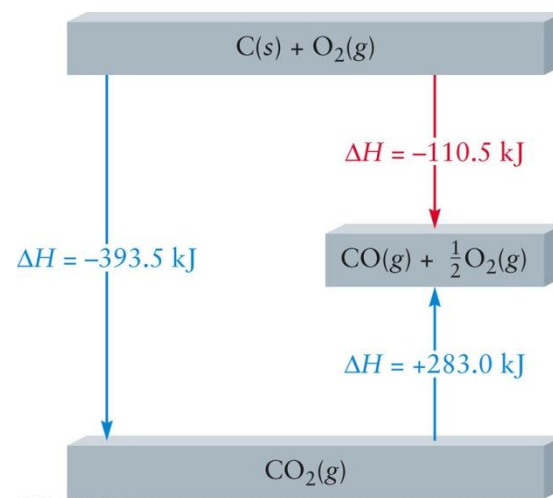
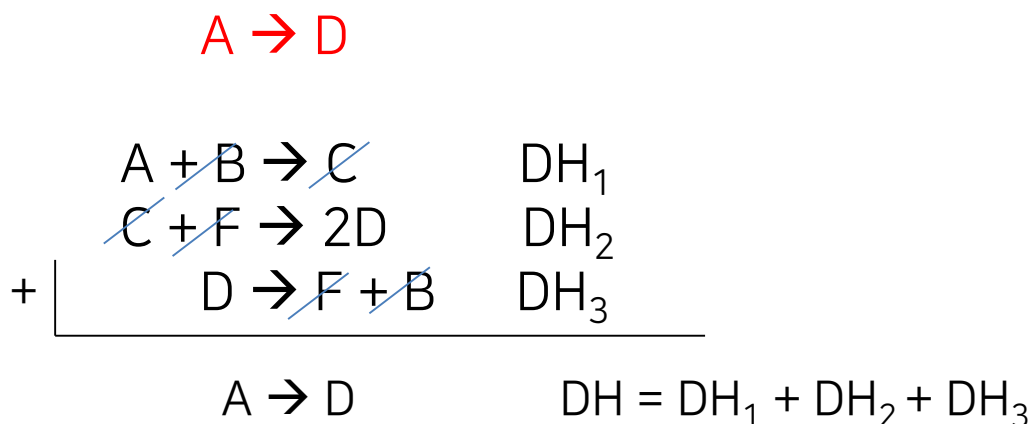
Standard state: pure form at exactly 1 bar (1 bar = 10^5 Pa)
(for solute in a liquid solution: 1 M)

Standard reaction enthalpy

$$(\Delta H^\circ) = H^\circ(\text{product}) - H^\circ(\text{reactant}) \quad (\text{generally at } 298.15 \text{ K} = 25^\circ \text{C})$$

Hess's Law

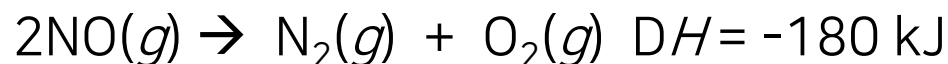
- For a given reaction, $A \rightarrow D$, reaction enthalpy, ΔH , can be obtained by:
 - Express the chemical reaction as a multiple steps of reactions with known ΔH 's:
 - Reaction enthalpy of the given reaction is the sum of the reaction enthalpies of these steps of reactions:



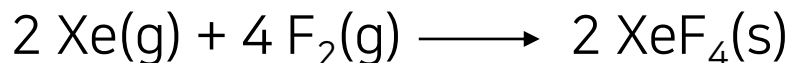
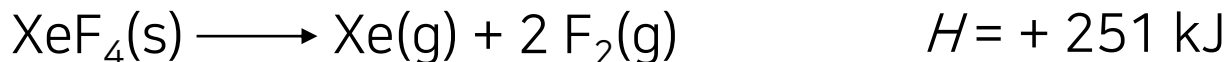
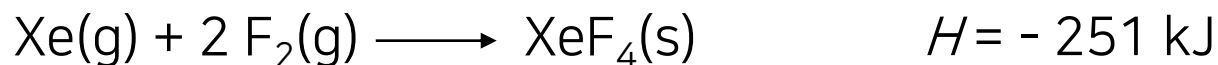
In other words, enthalpy is a **state function**.

Characteristics of enthalpy changes

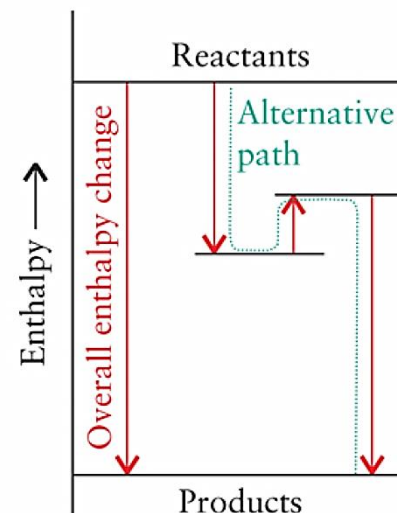
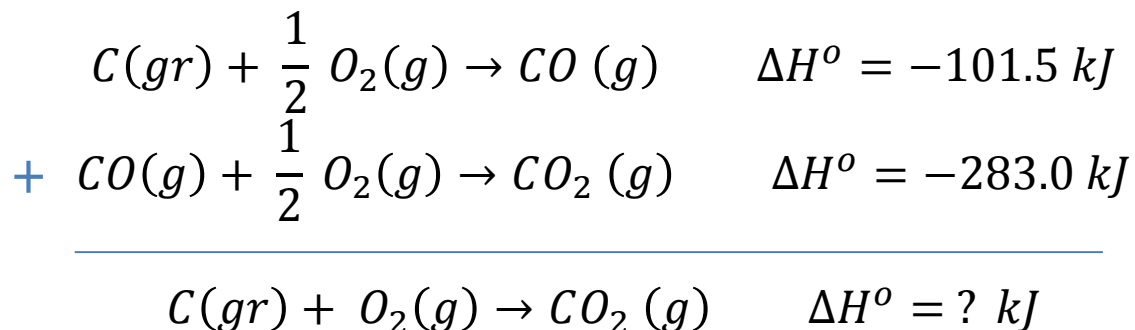
1. If a reaction is reversed, ΔH is also reversed.



2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.

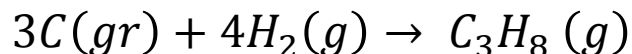


7.15. Combining Reaction Enthalpies: Hess's Law

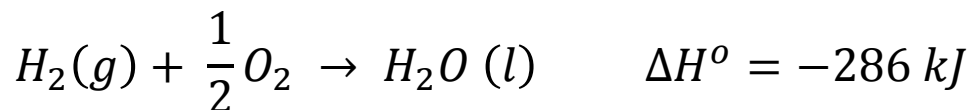
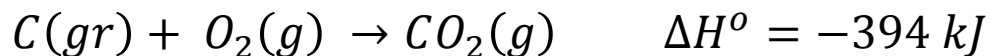
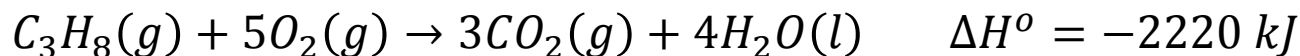


Example

Calculate the standard enthalpy change of the following reaction,



Using

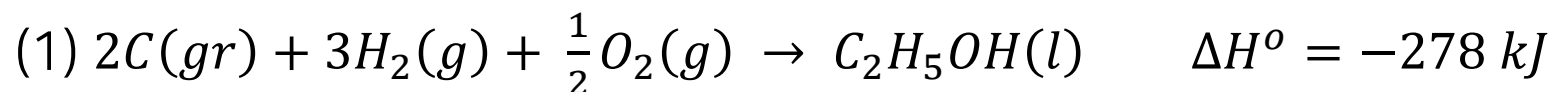


7.16. Standard Enthalpies of Formation

- Standard enthalpy of formation, ΔH_f°

: ΔH per mole of product formed from its elements in their most stable forms

-Examples



$$\rightarrow \Delta H_f^\circ(C_2H_5OH(l)) = -278 \text{ kJ/mol}$$

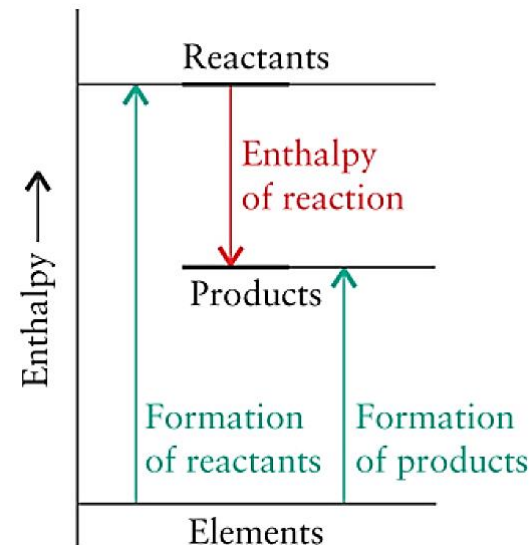


$$\rightarrow \Delta H_f^\circ(C(gr)) = 0 \frac{\text{kJ}}{\text{mol}}, \Delta H_f^\circ(C(dia)) = 1.9 \text{ kJ/mol}$$

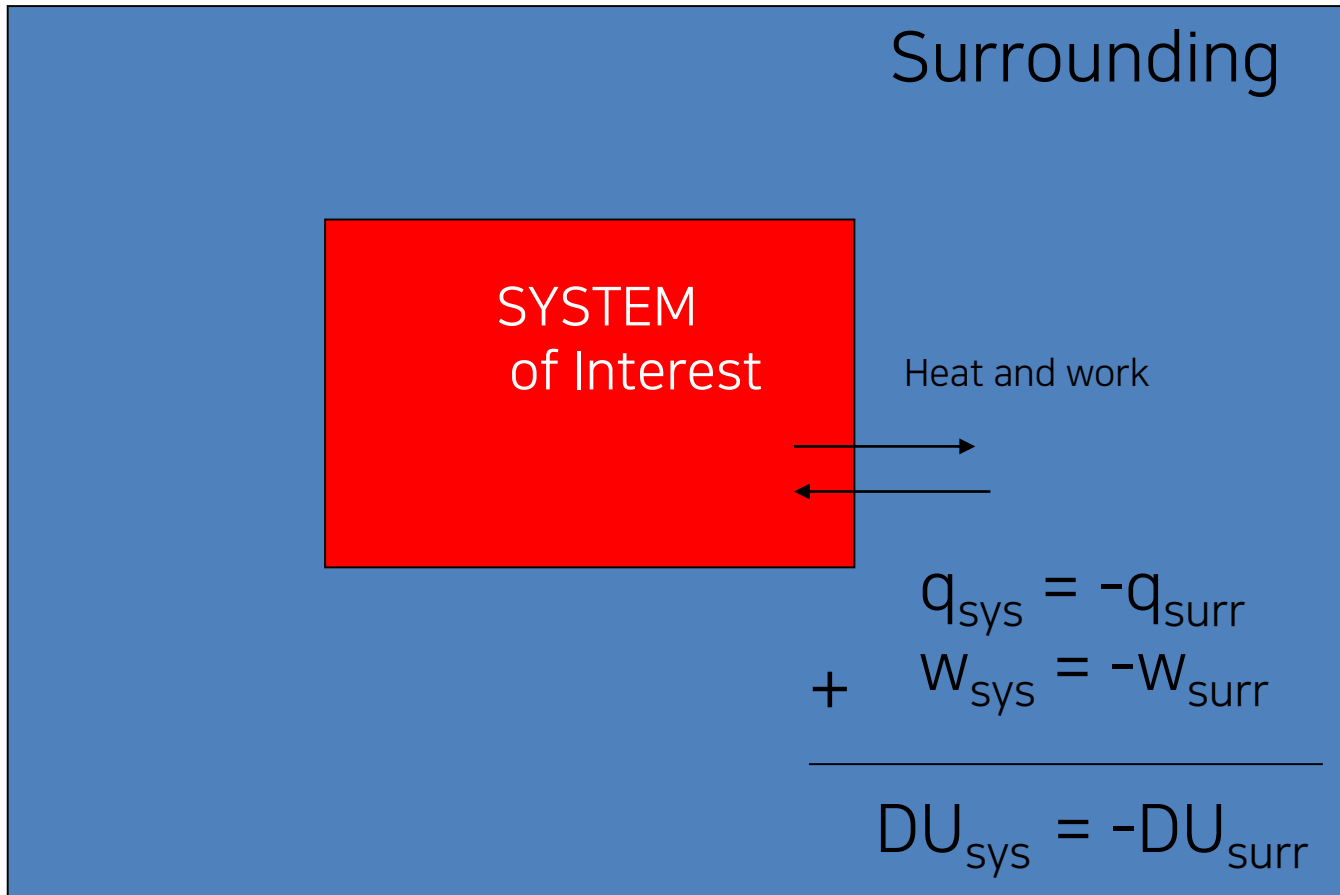
Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			Organic compounds		
ammonia	$\text{NH}_3(\text{g})$	-46.11	benzene	$\text{C}_6\text{H}_6(\text{l})$	+49.0
carbon dioxide	$\text{CO}_2(\text{g})$	-393.51	ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.69
carbon monoxide	$\text{CO}(\text{g})$	-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			
sodium chloride	$\text{NaCl}(\text{s})$	-411.15			
water	$\text{H}_2\text{O}(\text{l})$	-285.83			
	$\text{H}_2\text{O}(\text{g})$	-241.82			

- According to the *Hess's Law*

$$\Delta H^\circ = \sum_{\text{products}} n\Delta H_f^\circ - \sum_{\text{reactants}} n\Delta H_f^\circ$$



Review of Thermodynamics: System and Surrounding



1st law of thermodynamics: total energy, U is a STATE FUNCTION.

Review of Thermodynamics: Enthalpy

$$H = U + PV$$

Consider a chemical reaction occurring at constant external pressure, P_{ext} .

$$\begin{aligned}\Delta H_{\text{sys}} &= \Delta(U + PV) \\ &= \Delta U + P\Delta V \\ &= q + w + P\Delta V \\ &= q - P_{\text{ext}}\Delta V + P\Delta V \\ &= q + (P - P_{\text{ext}})\Delta V\end{aligned}$$

If the system is **mechanically in equilibrium**, $P = P_{\text{ext}}$,

$$\Delta H_{\text{sys}} = q$$