Topic 3
Thermodynamics

The study of transformations of energy

Heat $\leftrightarrow$ Work

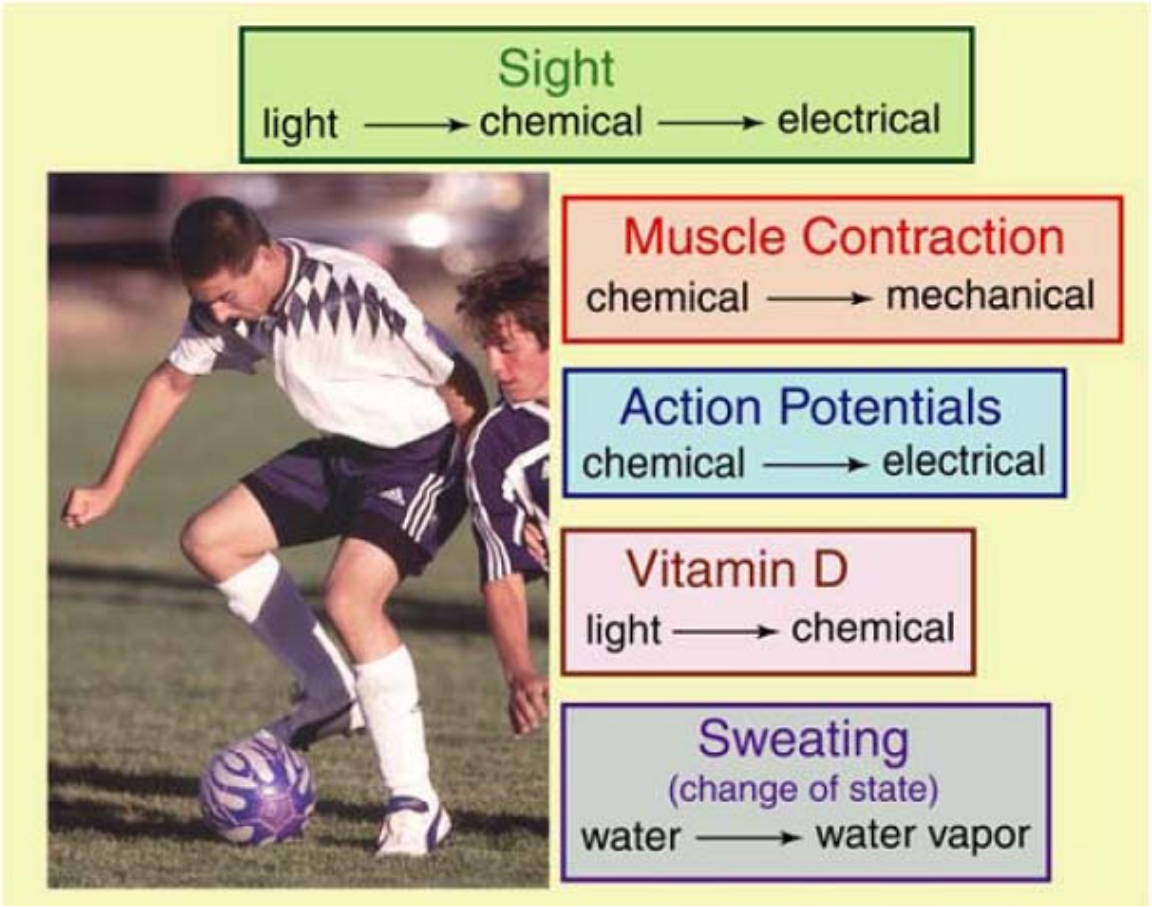
Thermochemistry: The study the heat changes of reactions

Electrochemistry: electricity and chemistry

Bioenergetics: energy in living organisms

Two laws of bioenergetics

- The law of conservation of energy



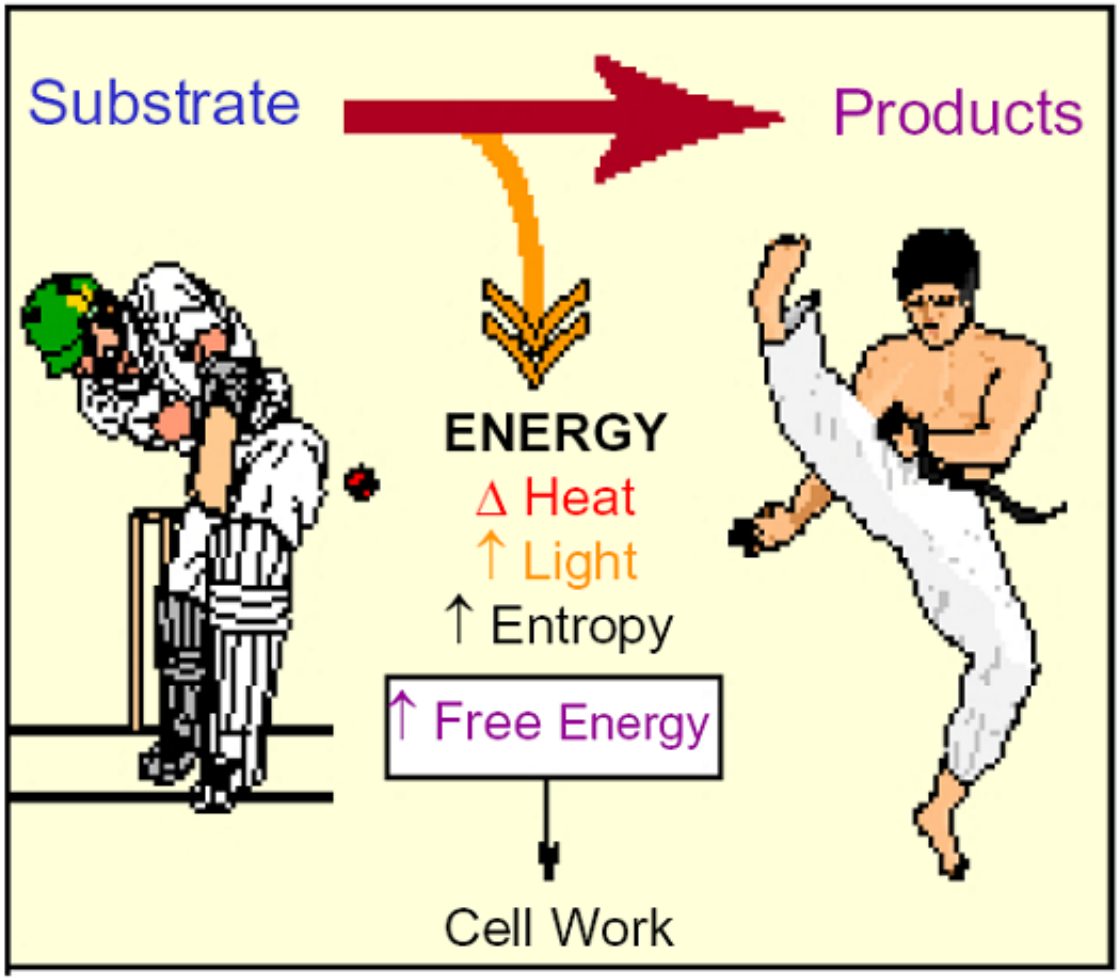
Key concepts

E. can NOT be created or destroyed,

But

can be changed from one to another

- Entropy & the 2nd law of thermodynamics



Key concepts

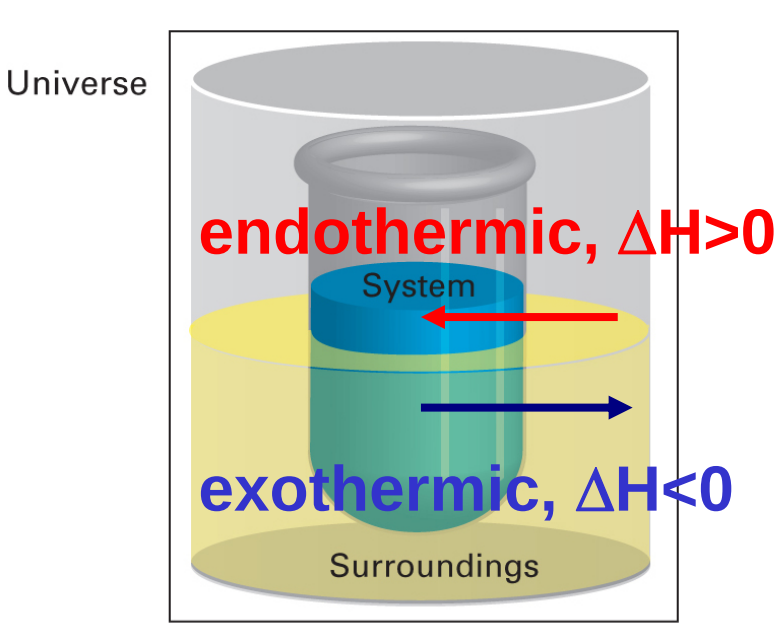
E transfer will always proceed in the direction of increased entropy & the release of "free energy"

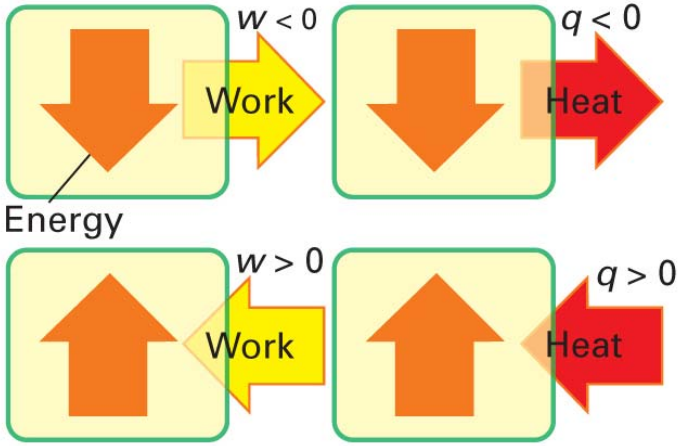
The conservation of energy

- Energy is the capacity to do work or to product heat.
  - Work is done to achieve motion against an opposing force.
  - Heat is energy in transit as a result of a temperature difference.
- All forms of energy can be interconverted.
- The total energy in the universe remain constant.

Systems and surroundings

- **System** – part of the universe on which we wish to focus attention. ⇒ (reactants + products)
- **Surroundings** – include everything else in the universe. ⇒ rxn's container, the room ……





ΔU = q + w
(internal energy of a system)

Classify each process as exothermic or endothermic. Explain. The system is underlined in each example.

Exo a) Your hand gets cold when you touch ice.

Endo b) The ice gets warmer when you touch it.

Endo c) Water boils in a kettle being heated on a stove.

Exo d) Water vapor condenses on a cold pipe.

Endo e) Ice cream melts.

For each of the following, define a system and its surroundings and give the direction of energy transfer.

a) Methane is burning in a Bunsen burner in a laboratory.

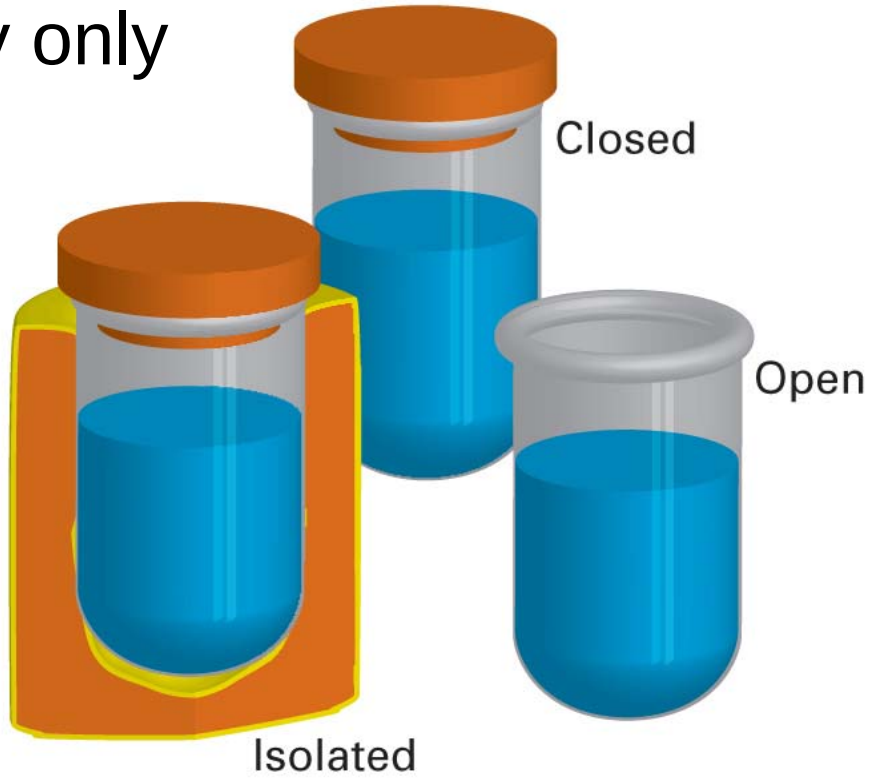
b) Water drops, sitting on your skin after swimming, evaporate.

Hydrogen gas and oxygen gas react violently to form water. Explain.

- Which is lower in energy: a mixture of hydrogen and oxygen gases, or water?

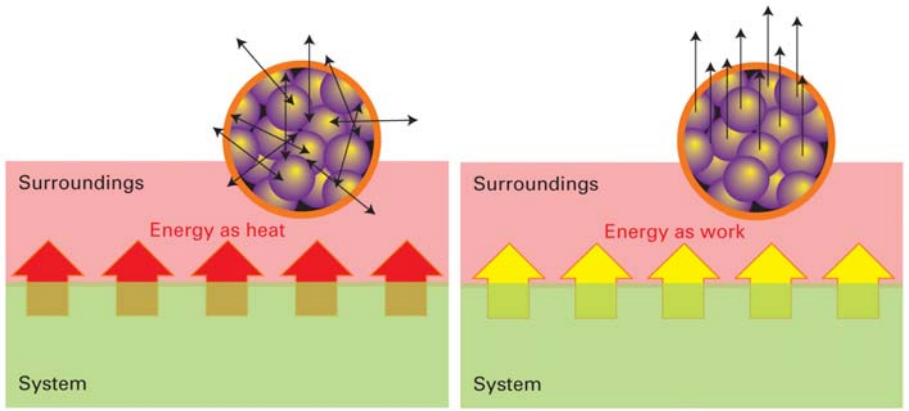
Three types of systems

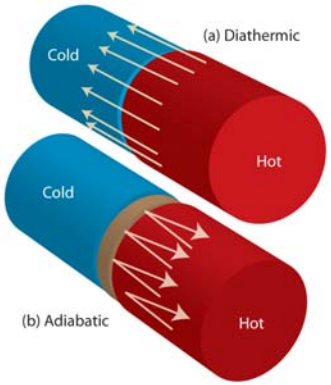
- Open: exchange both energy and matter with its surroundings.
- Close: exchange energy only
- Isolated: nothing



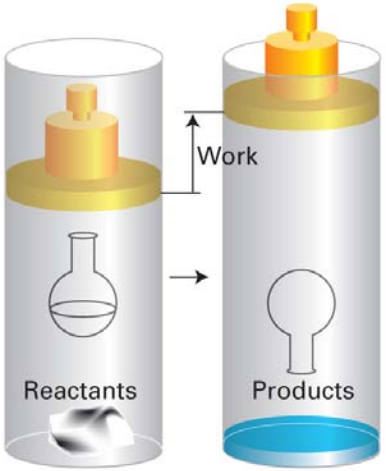
Work and Heat

- w & q are modes of transfer of energy, not forms of energy.
  - w: uniform motion
  - q: random motion
    - diathermic
    - adiabatic





- **$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$**
  - How to detect the transfer energy? w? q?



The measurement of work

$| w | = | F \times d | = | P \times A \times \Delta h | = | P\Delta V |$

expansion work $\Delta V > 0$ & $w < 0$

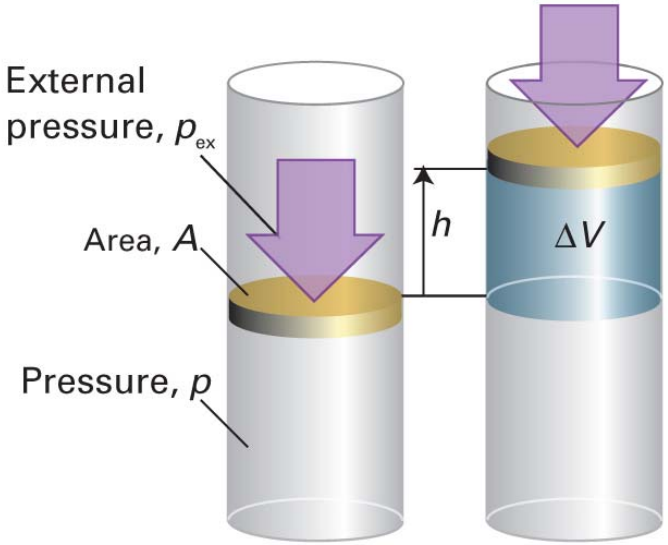
$\Rightarrow w = -P\Delta V = -RT\Delta n(g)$

For the reversible expansion

$W = -\int PdV$

For a isothermal perfect gas

$w = -nRT \ln (V_f / V_i)$



Ex: Work done by a chemical reaction

Determine work done by 1 mol propane & its rxn as follow:

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

The measurement of heat

- Heat capacity: $C = q/\Delta T$ $\quad q = C\,\Delta T$
- molar heat capacity： C_m ⇨ $JK^{-1}mol^{-1}$ (C_s?)
- Calorimeter: way to measure q transfer
- Heat influx during expansion

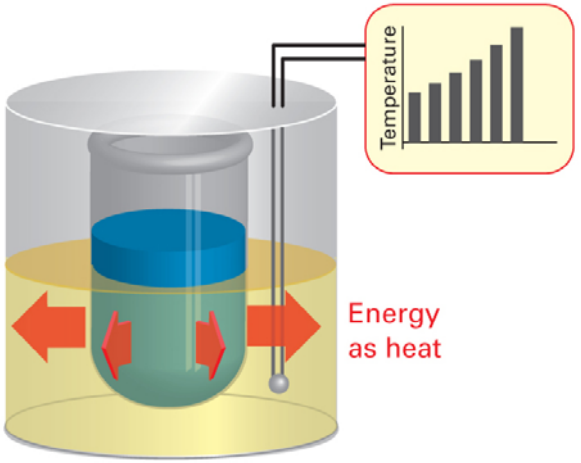
  For isothermal perfect gas

  $q = -w$

  & for reversible perfect gas

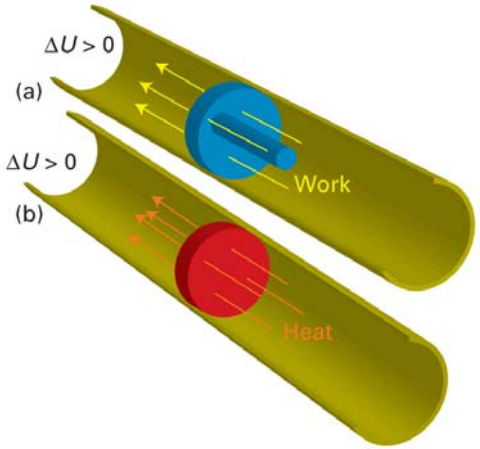
  $q = \mathbf{nRT\ ln\ (V_f / V_i)}$

- w & q are Path function



Internal energy (U)

- the sum of all the kinetic and potential energy of all atoms, ions, and molecules in the system.
- Only can deal with **ΔU**, not with **U** itself.
- $\Delta U = w + q$



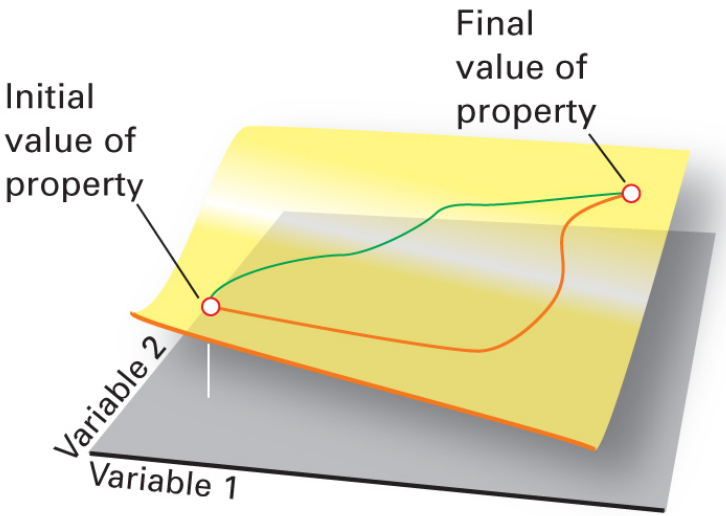
Ex: What is ΔU?

(1) A perfect gas is isothermal expansion.

(2) Someone does 622 kJ of work on exercise bicycle and losses 82 kJ of energy as heat. Disregard any matter loss by perspiration.

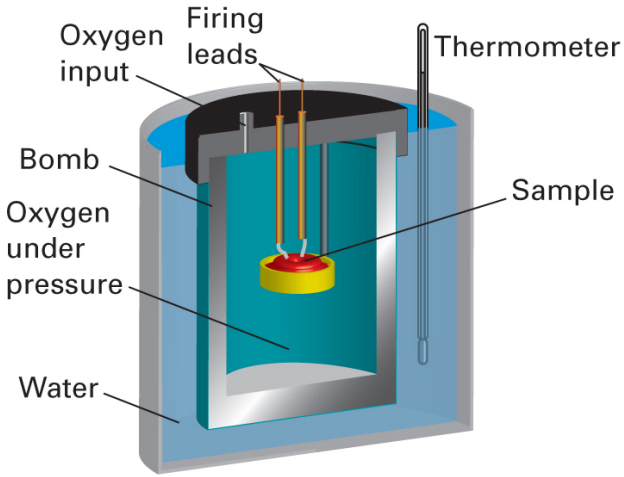
Internal energy as a state function

- State function:
  Path independence
- 1st law:
  for an isolated system
  U is constant



- At constant volume,
  non-expansion work

$$\Delta U = q_v + \cancel{w}$$
$$= C_v \Delta T$$



Enthalpy

Ex: the oxidation of a fat in a body:

For consumption of 1g fat at 25°C

$2C_{57}H_{110}O_6(s) + 163O_2(g) \rightarrow 114\ CO_2(g) + 110\ H_2O(l)$

ΔV = ?, w > 0 or <0?

H of a system, U of the system avoiding w.

Enthalpy

(1) $H = U + PV \Rightarrow \Delta H = \Delta U + \Delta (PV)$

$\hookrightarrow$ state function $\Delta H = H_f - H_i$

(2) at const. pressure :

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

$$\Rightarrow q_p = \Delta U + P\Delta V$$

(3) from (1) & (2)

$$\Delta H = q_p = C_p \Delta T$$

At const. P, the change in enthalpy (ΔH) of the sys. is equal to the **energy flow as heat**.

(4) for chemical rxn :

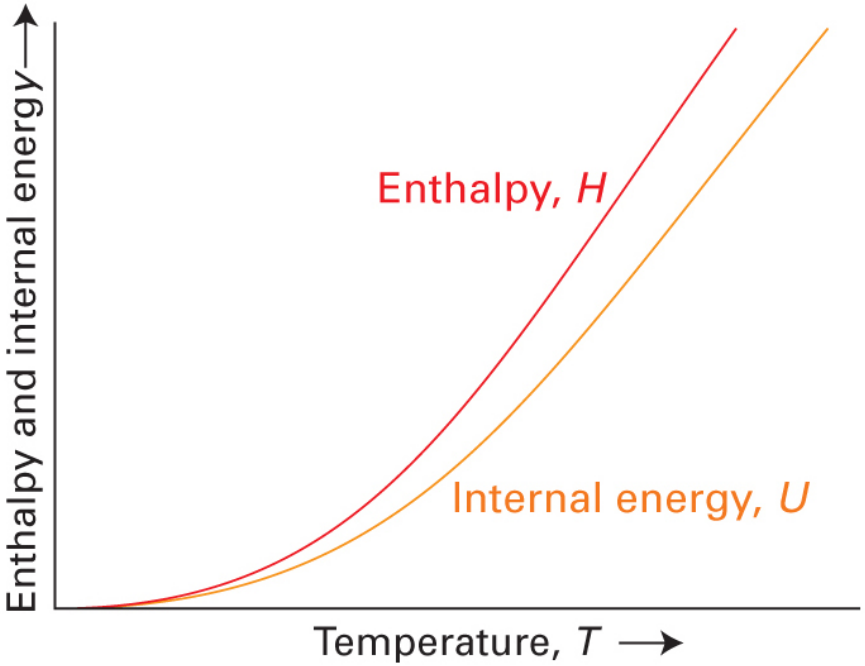
$$\Delta H = H_f - H_i$$

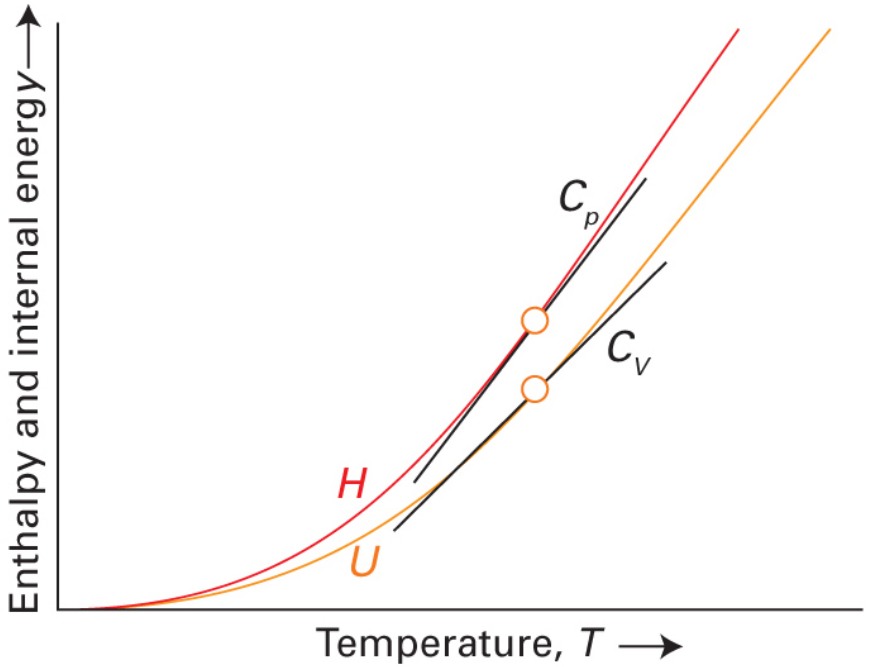
$$= H_{\text{products}} - H_{\text{reactants}}$$

$\Delta H > 0$ endothermic rxn

$\Delta H < 0$ exothermic rxn

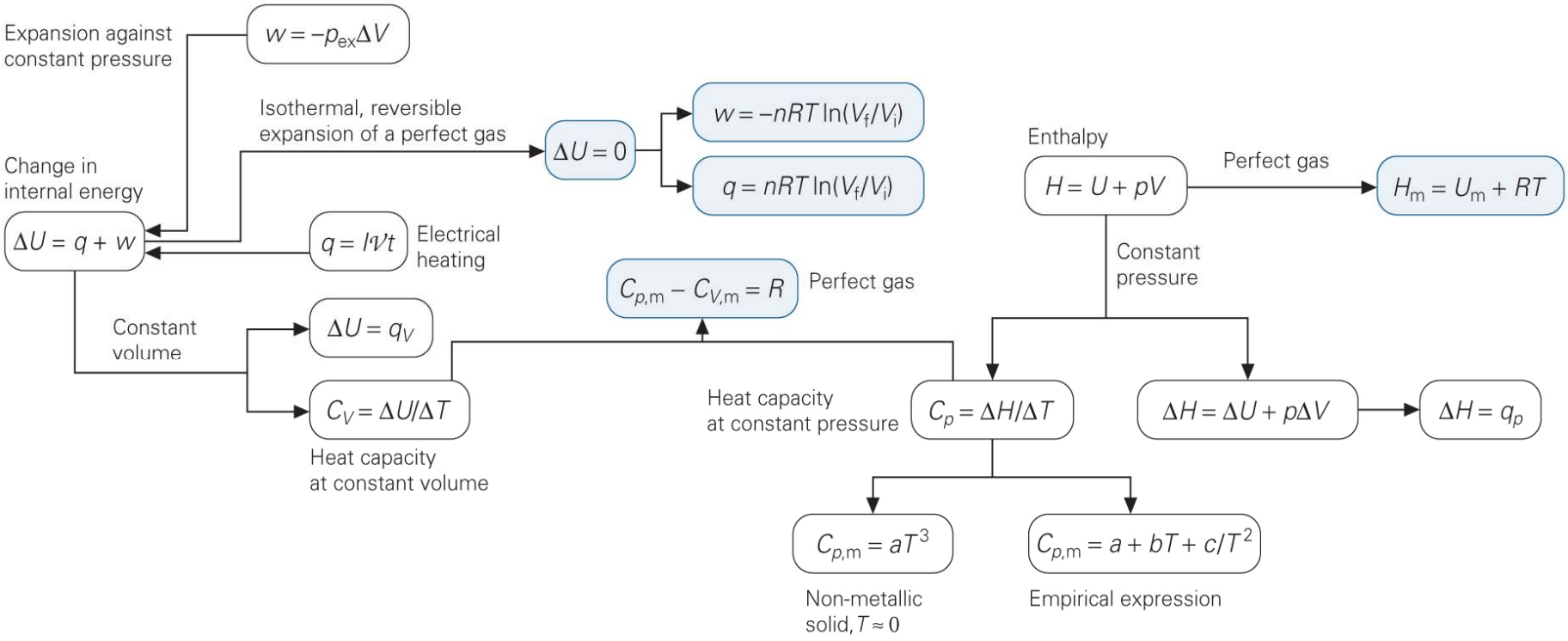
The T variation of the H





- $H = C_p\Delta T > U = C_v\Delta T$
- for perfect gas, $C_p - C_v = R$

Road map of key equation



Blue boxes are relations for perfect gases.

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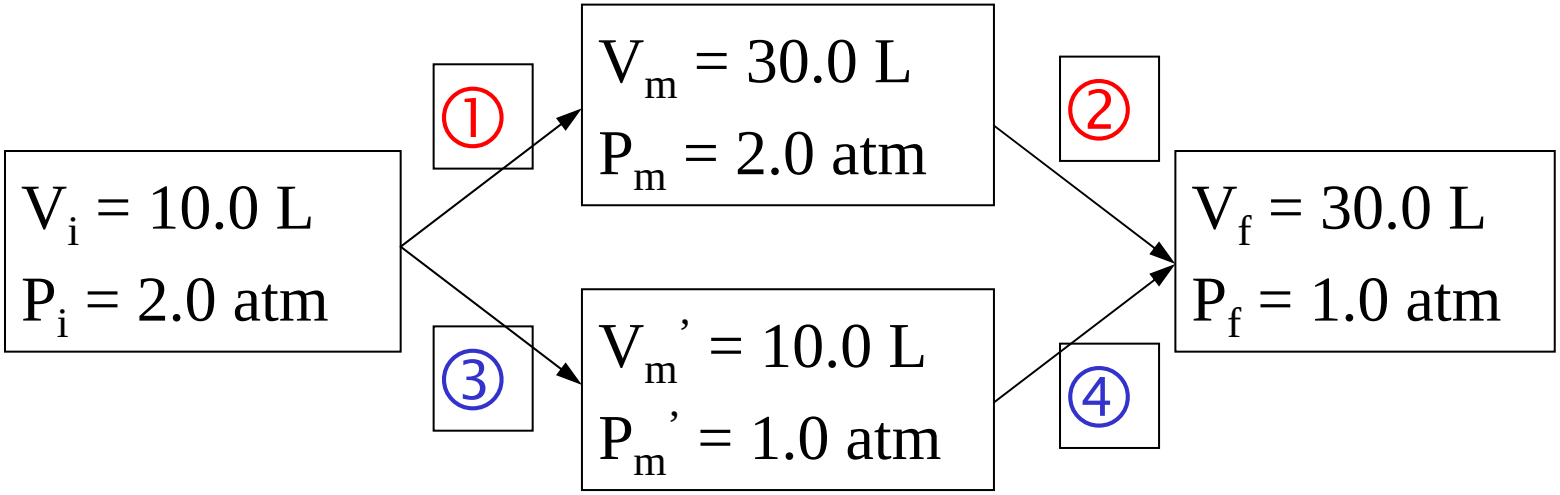
Question: Find w, q, ΔU, ΔH for the path up & down.



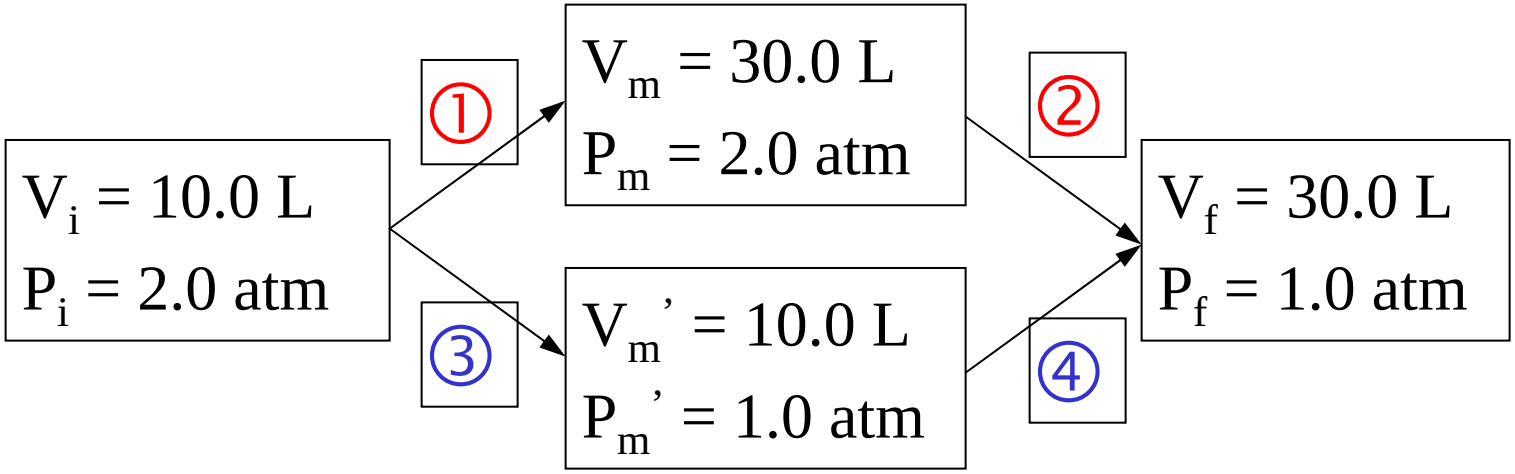
① & ④ $\Rightarrow$ $\Delta P = 0$

$$w = -P\Delta V$$

$$q = q_P = \Delta H = nC_P\Delta T$$

$$\Delta U = q + w = nC_V\Delta T$$

where $\Delta T = \Delta PV/nR$



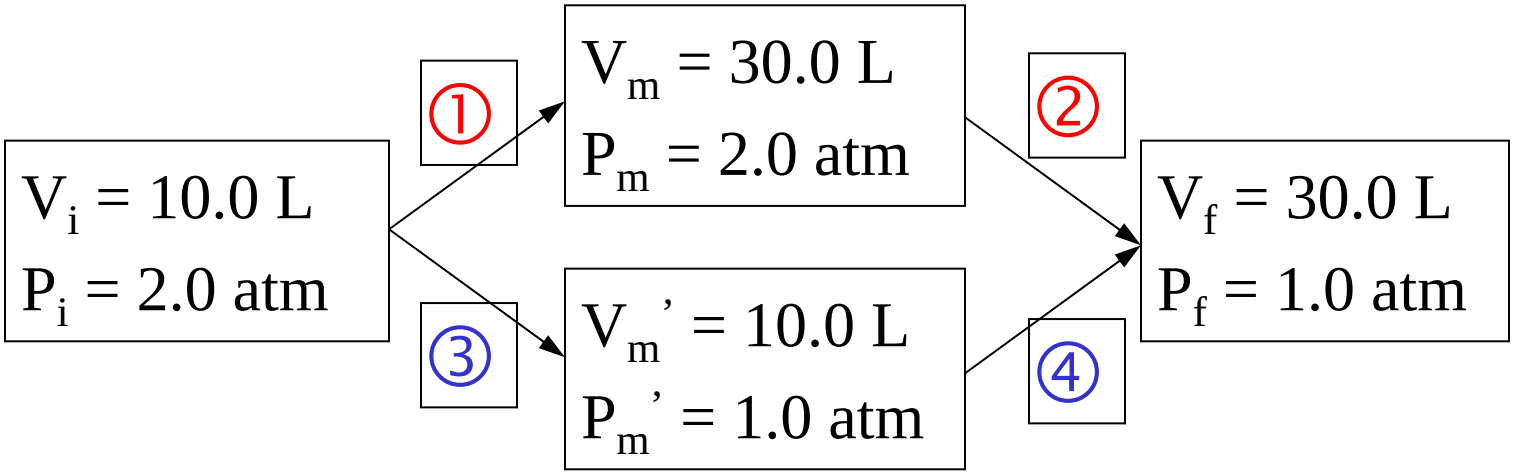
② & ③ $\Rightarrow$ $\Delta V = 0$

$w = 0$

$q = q_V = \Delta E = nC_V\Delta T$

$\Delta H = nC_P\Delta T$

where $\Delta T = \Delta PV/nR$



summary

$w_{up} \neq w_{down}$
$q_{up} \neq q_{down}$
$\Rightarrow$ Path function

$\Delta U_{up} = \Delta U_{down}$
$\Delta H_{up} = \Delta H_{down}$
$\Rightarrow$ State functions

Homework (3/17/2014)

- Discussion:
  - 2.9
- Exercises:
  - 2.3, 2.6, 2.7, 2.10, 2.15, 2.23

Applications of the first law
Enthalpy

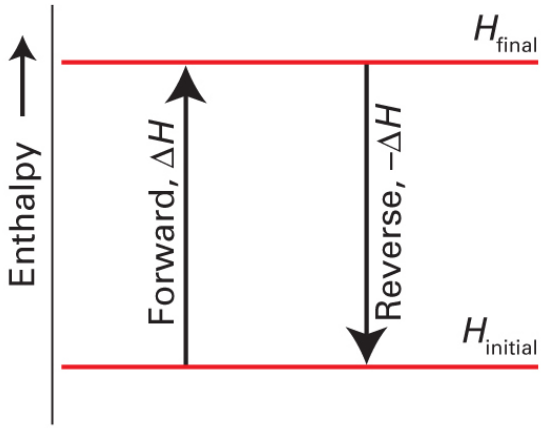
(1) H is a state function.

$$\Delta H = H_f - H_i$$

(2) $A + B \rightarrow C + D \qquad \Delta H$

$C + D \rightarrow A + B \qquad -\Delta H$

(3) $2A + 2B \rightarrow 2C + 2D \qquad 2\Delta H$



Standard enthalpy

(1) ΔH depend on Temp. & Pressure

standard $\Rightarrow$ 25℃ 1atm

(2) ΔH^{o}_{rxn} : standard H change in reaction

(3) ΔH^{o}_{f} : ΔH^{o} of a rxn for the formation of one mole of a compound directly from its elements.

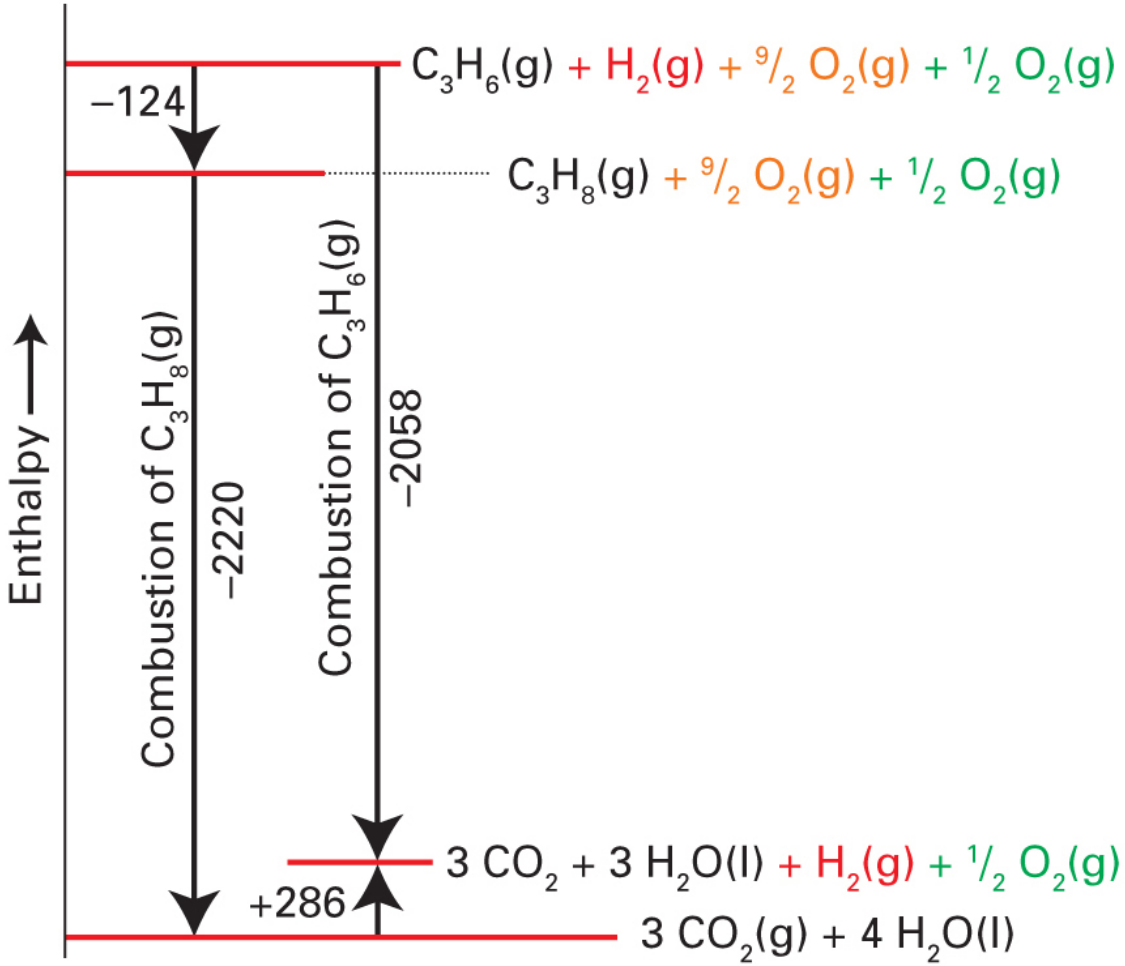
(4) $\triangle H^{\circ}_{f} = 0$ for all the elements

(5) $\Delta H^{o}_{rxn} = \Sigma \Delta H^{o}_{f}$ (products) $-$ $\Sigma \Delta H^{o}_{f}$ (reactants)

The combination of reaction: using Hess's law

For propene

ΔH^o = ?



The combination of reaction:

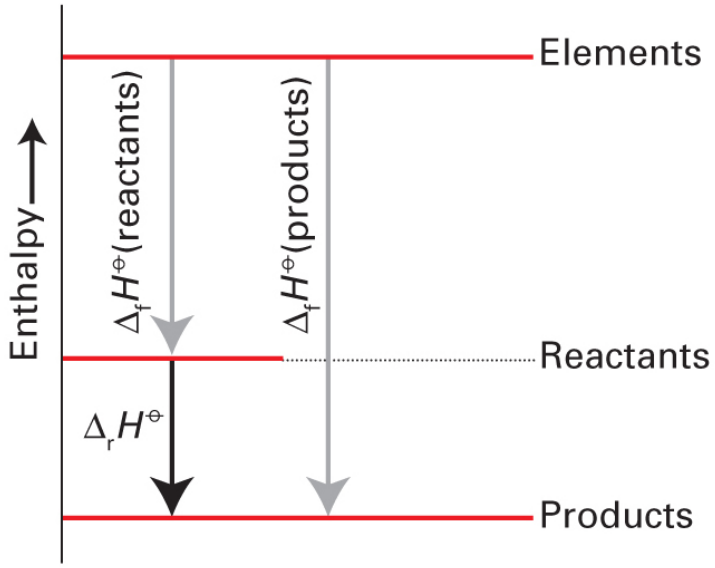
$2B_{(S)} + 3H_{2(g)} \rightarrow B_2H_{6(g)} \quad \Delta H^o = ?$

Given:

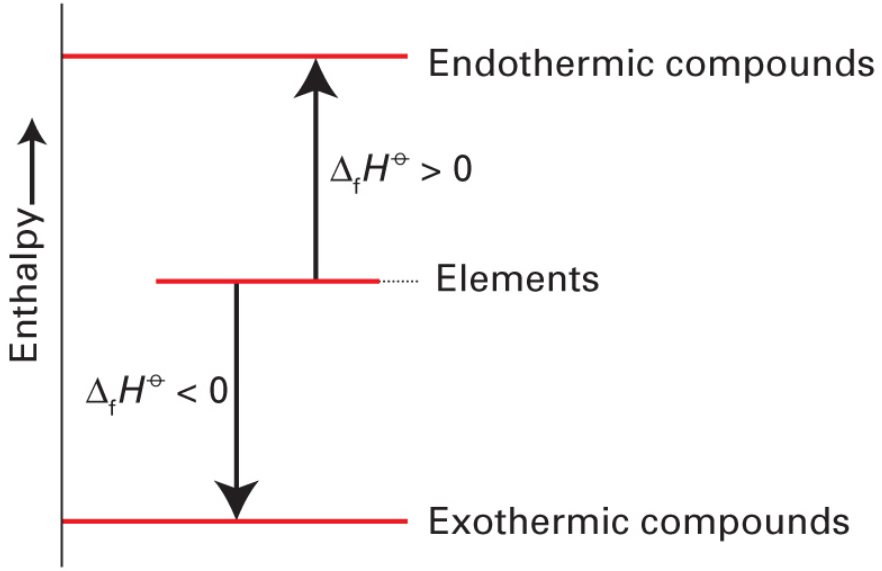
	ΔH^o
(a) $2B_{(S)} + 3/2\ O_{2(g)} \rightarrow B_2O_{3\,(S)}$	-1273 kJ
(b) $B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(S)} + 3H_2O_{(g)}$	-2035 KJ
(c) $H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(l)}$	-286 KJ
(d) $H_2O_{(l)} \rightarrow H_2O_{(g)}$	44 KJ

Solve: (a) $-$ (b) + 3(C) + 3(d)

H of reaction



Endothermic & Exothermic



Homework (3/17/2014)

- Exercises:
  - 3.28
  - 3.32

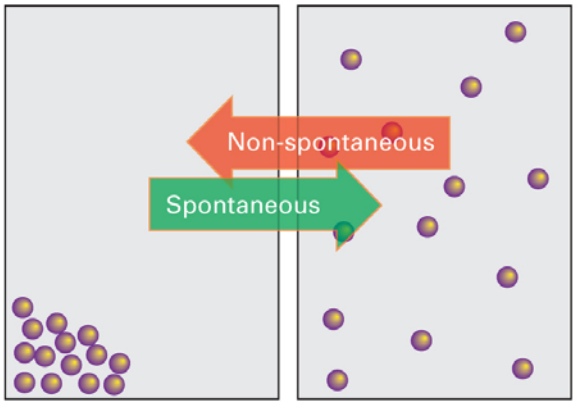
The second law

(1) spontaneous process :

it occurs without outside intervention.

(2) spontaneous rxn & speed

$\Rightarrow$ thermodynamics vs kinetics



the science of E transfer predict occur

vs

study of the rates of rxn why somes are fast or slow?

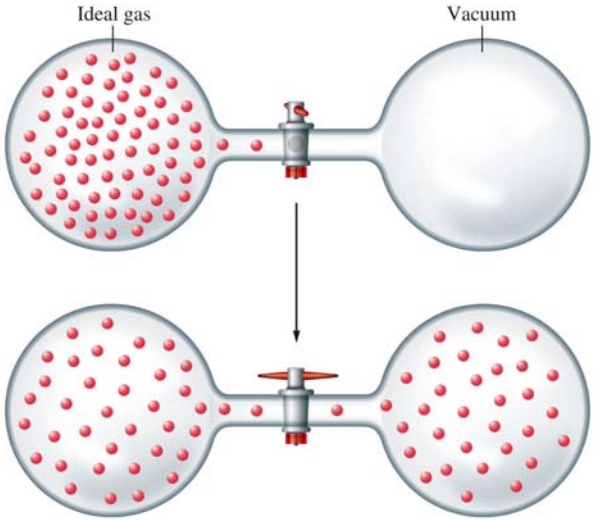
ex. $2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$

Product favored $\longrightarrow$; $\longleftarrow$ reactant favored

(spontaneous rxn)

Spontaneous reaction

Nonspontaneous reaction



(3) why product - favored ?

$\Delta H < 0 \Rightarrow$ energy ↓ ?

(exothermic)

How about $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H > 0$ at 0℃

(4) something else ! ⇒ Entropy (*S*)

S = the driving force for a spontaneous process is an increase in the entropy of the universe.

= a measure of randomness or disorder of a system the great the randomness, the greater ***S***.

= the number of arrangements ⇒ probability the higher probability, the higher ***S***

(5) $S \geq 0$ ($S = 0$ for a perfect crystal at 0 K)

(6) $\Delta S = S_f - S_i$

(7) generalization :

a) $S_{(g)} >> S_{(l)} > S_{(s)}$

b) S : more complex molecules > simpler

(ex) : $CH_3CH_2CH_3 > CH_3CH_3 > CH_4$

c) S : ionic solid $_{\text{(weaker force)}}$ > ionic solid $_{\text{(stronger force)}}$

(ex) : $NaF_{(s)} > MgO_{(s)}$

d) liq and solid dissolve in a solvent $\Delta S > 0$

gas dissolve in a solvent $\Delta S < 0$

Predict the sign of ΔS for each of the following, and explain:

+ a) The evaporation of alcohol
– b) The freezing of water
– c) Compressing an ideal gas at constant temperature
+ d) Heating an ideal gas at constant pressure
+ e) Dissolving NaCl in water

Entropy and the second law

- Suniverse

  $\Delta S_{univ.} > 0$ for spontaneous rxn

  $\Delta S_{univ.} = \Delta S_{sys.} + \Delta S_{surr.}$

- For quantitatively useful:
- $\Delta S = q_{rev}/T$ at cont. T (isothermal)
- $\Delta S = nR \ln(V_f/V_i)\ q_{rev}/T$ for perfect gas

In any spontaneous process, there is always an increase in the entropy of the universe

$\Delta S_{univ.} > 0$ for spontaneous rxn

$\Delta S_{univ.} = \Delta S_{sys.} + \Delta S_{surr.}$

System: rxn $R \rightleftharpoons P$

- $\Delta S_{univ.} > 0$ rxn $\rightarrow$
- $\Delta S_{univ} < 0$ rxn $\leftarrow$
- $\Delta S_{univ} = 0$ rxn at equilibrium

ex) $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

(1) System

(l) → (g) 18 *ml* (1 mol) → 31 L

$\Delta S_{sys.} > 0$

(2) Surrounding

a) **sign** (+ or −) depend on “heat flow”

exothermic process ⇒ $\Delta S_{surr} > 0$

endothermic process ⇒ $\Delta S_{surr} < 0$

b) **magnitude** depend on the temp.

$T \geq 100\ ^oC$ for rxn $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$ const. T & P

$q_p = |\Delta H|$

(3) $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

TABLE 17.3 › Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Process Spontaneous?
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

ΔS_{surr}

- The sign of ΔS_{surr} depends on the direction of the heat flow.
- The magnitude of ΔS_{surr} depends on the temperature.

Exothermic process:	$\Delta S_{surr} = +\dfrac{\text{quantity of heat (J)}}{\text{temperature (K)}}$
Endothermic process:	$\Delta S_{surr} = -\dfrac{\text{quantity of heat (J)}}{\text{temperature (K)}}$

The Gibbs energy
focusing on the system

G is a thermodynamic function that gives information about the spontaneity of the system.

$G = H - TS$ (for system)

$\Delta G = \Delta H - T\Delta S_{sys}$ (const. T & P)

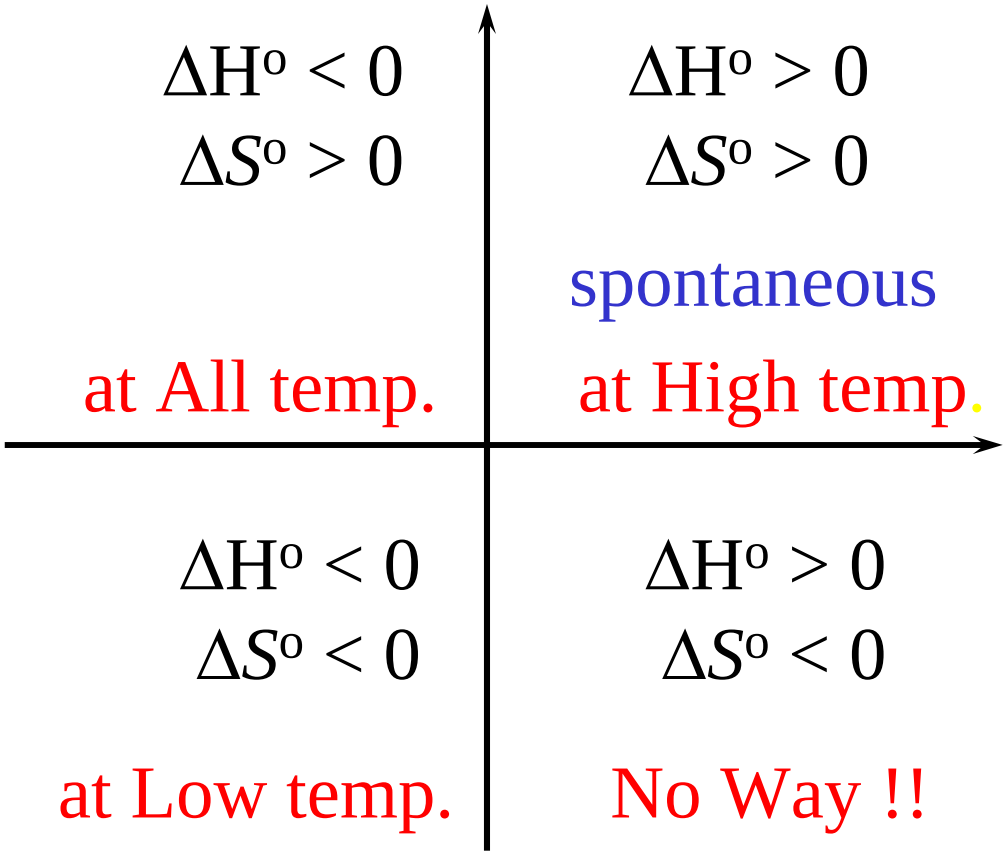
$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S_{sys}$$

$$-\frac{\Delta G}{T} = \Delta S_{surr} + \Delta S_{sys} = \Delta S_{univ}$$

$$\Delta S_{univ} = -\frac{\Delta G}{T}$$

$\Delta G < 0$	$R \rightarrow P$	spontaneou
$\Delta G > 0$	$R \leftarrow P$	nonspontaneous
$\Delta G = 0$	$R \leftrightarrows P$	equilibrium

$$\Delta G = \Delta H - T\Delta S_{sys}$$



A liquid is vaporized at its boiling point.
Predict the signs of:

w	–
q	+
ΔH	+
ΔS	+
ΔS_{surr}	–
ΔG	0

Explain your answers.

Exercise

The value of $\Delta H_{vaporization}$ of substance X is 45.7 kJ/mol, and its normal boiling point is 72.5°C.

Calculate ΔS, ΔS_{surr}, and ΔG for the vaporization of one mole of this substance at 72.5°C and 1 atm.

$\Delta S = 132$ J/K·mol

$\Delta S_{surr} = -132$ J/K·mol

$\Delta G = 0$ kJ/mol

Gas A_2 reacts with gas B_2 to form gas AB at constant temperature and pressure. The bond energy of AB is much greater than that of either reactant.

Predict the signs of:

ΔH	ΔS_{surr}	ΔS	ΔS_{univ}
–	+	0	+

Explain.

(1) ex.

① $N_{2\,(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$\Delta S < 0$

② $H_{2(g)} \rightarrow 2H_{(g)}$

③ $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$

(2) enthalpy (H) (at const. P)

ΔH determines a rxn { exothermic / endothermic

(3) free energy (G) (at const. T & P)

ΔG determines a rxn { spontaneous / nonspontaneous / equilibrium

(4) $S \rightarrow$ absolute values $\Delta S_{T_1 \rightarrow T_2}$

$S = 0$ for a perfect crystal at 0 ^{o}K

3rd law of thermodynamics

(5) standard entropy S^{o} (298 K & 1 atm)

$$\Delta S^{o}_{rxn} = \sum S^{o}_{products} - \sum S^{o}_{reactants}$$

Standard G

(1) ΔH^o ： measured by calorimeter

(2) ΔG^o ： standard free energy change

25 ℃ ， 1 atm

① The more negative the value of ΔG^o , the further a rxn will go to the right.

② calculated by $\Delta G^o = \Delta H^o - T\,\Delta S^o$

③ ΔG^o_{rxn} can be calculated by using Hess's law.

④ ΔG^o_f = standard free energy of formation

$$\Delta G^o_{rxn} = \sum \Delta G^o_{f\ (products)} - \sum \Delta G^o_{f\ (reactant)}$$

$\Delta G^o_f = 0$ for elements

Ex: ΔG^{o}_{rxn} calculated using Hess's law

$$C^{\text{diamond}}_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} \qquad \Delta G^{o} = -397\text{kJ}$$

$$C^{\text{graphite}}_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} \qquad \Delta G^{o} = -394\text{kJ}$$

$$\Rightarrow \quad C^{\text{diamond}}_{(s)} \rightarrow C^{\text{graphite}}_{(s)} \qquad \Delta G^{o} = -3\text{kJ}$$

$\downarrow$

kinetically stable

thermodynamically unstable

rxn $\leftarrow$ when high temp.

Concept Check

A stable diatomic molecule spontaneously forms from its atoms.

Predict the signs of:

ΔH°	ΔS°	ΔG°
–	–	–

Explain.

Free Energy and Pressure

$$G = G^{\circ} + RT \ln(P)$$

or

$$\Delta G = \Delta G^{\circ} + RT \ln(Q)$$

(1) $S_{\text{large V}} > S_{\text{small V}} \Rightarrow S_{\text{low P}} > S_{\text{high P}}$

$G = G^{o} + RT\,ln(P)$

G^{o} : the gas at the P = 1 atm

G : the gas at the P = P

ex. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$\Delta G = \Sigma G_{\text{products}} - \Sigma G_{\text{reactants}}$

$= 2G_{NH_3} - (G_{N_2} + 3G_{H_2})$

where $G_{NH_3} = G^{o}_{NH_3} + RT\,ln(P_{NH_3})$

$G_{N_2} = ?$

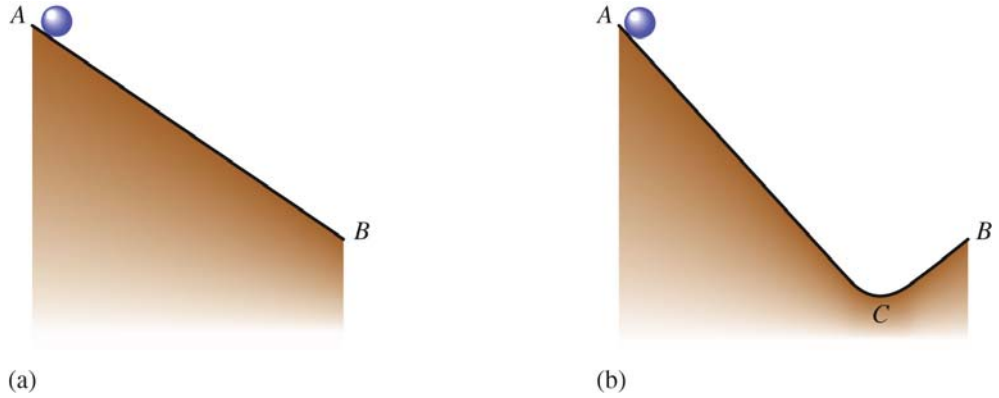
$G_{H_2} = ?$

$$\Delta G = (2G^{o}_{NH_3} - G^{o}_{N_2} - 3G^{o}_{H_2}) + RT\,[2\ln(P_{NH_3}) - \ln(P_{N_2}) - 3\ln(P_{H_2})]$$

$$= \Delta G^{o} + RT\ln[(P_{NH_3})^2 / (P_{N_2})(P_{H_2})^3]$$

$$\Delta G = \Delta G^{o} + RT\ln Q$$

(2) The meaning of ΔG for a chemical rxn.



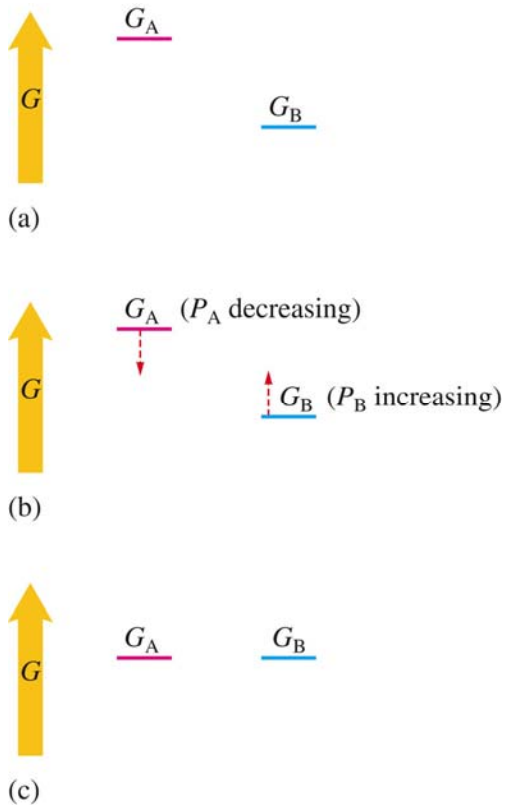
- The equilibrium point occurs at the lowest value of free energy available to the reaction system.

$$\triangle G = 0 = \triangle G^{\circ} + RT \ln(K)$$

$$\triangle G^{\circ} = -RT \ln(K)$$

(1) $A_{(g)} \leftrightarrows B_{(g)}$

at equilibrium : $G_{products} = G_{reactants}$



$\Rightarrow \quad \Delta G = G_P - G_r = 0$

& $\quad \Delta G = \Delta G^o + RT\ln Q$

i.e. $\Delta G = \Delta G^o + RT\ln k = 0$ (equilibrium)

$\Delta G^o = -RT\ln k$

① $\Delta G^o = 0 \rightarrow k = 1$

② $\Delta G^o < 0 \rightarrow k > 1$ products favor

③ $\Delta G^o > 0 \rightarrow k < 1$ reactants favor

(2) Temp. dependence

$$\Delta G^o = -RT\ln K = \Delta H^o - T\Delta S^o$$

$$\ln K = -\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$$

$y = mx + b$

(ln K) vs. (1/T)

ex.

$$N_{2\,(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)}$$

$\Delta G^o = -33.3$ kJ at 25°C

(a) $P_{NH_3} = 1.00$, $P_{N_2} = 1.47$ atm,

$P_{H_2} = 1.00 \times 10^{-2}$ atm

predict the rxn direction to reach equilibrium?

Solution : $\Delta G = \Delta G^o + RT\ln Q$

ex.

Calculate k for the follow rxn at 25 ^{o}C

$$4Fe_{(s)} + 3O_{2(g)} \leftrightarrows 2Fe_2O_{3(s)}$$

ΔH^{o}_{f} (kJ/mol)	0	0	-826
ΔS^{o}_{f} (J/kmol)	27	205	90

Solution : $\Delta G = \Delta G^{o} + RT\ln Q$

$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$

ex.

Calculate k for

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \xrightarrow{k} NH_{3(g)} \qquad \Delta H^{o} = -92\ kJ$$

$k = 3.7 \times 10^{-6}$ at T = 900 K

k = ? at T = 550 K