Review: Chapter5 Thermochemistry
Chapter 19 Chemical *Thermodynamics*

Outlines

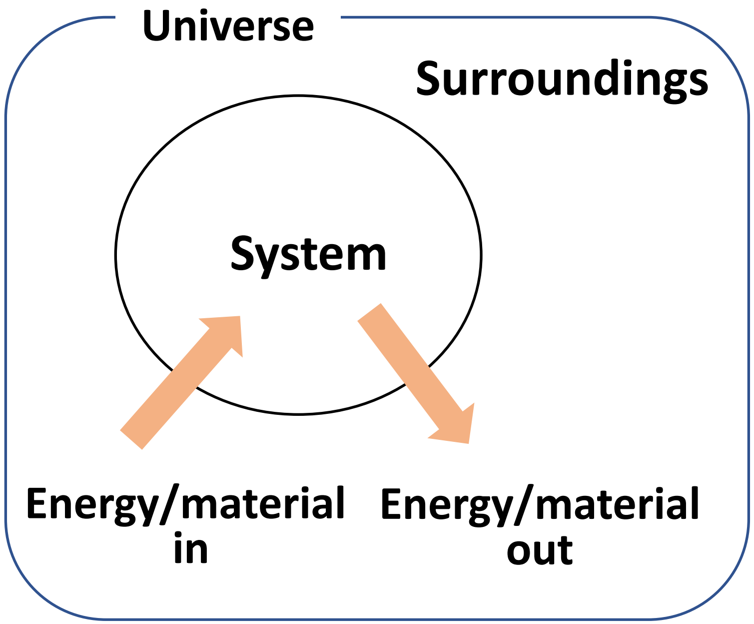
Thermodynamics is a wonderful theory. By this, we can explain and predict why a certain reaction happens in a certain direction.

- First law of thermodynamics
- Energy, heat, and work.
- Enthalpy
- Heat capacity

First Law of Thermodynamics

- Energy is neither created nor destroyed (the law of energy conservation).
- In other words:

$$\Delta E_{\text{Universe}} = \Delta E_{\text{System}} + \Delta E_{\text{Surrounding}}$$



Universe

Surroundings

System

Energy/material in

Energy/material out

Open system
Energy exchange (O)
Material exchange (O)

Closed system
Energy exchange (O)
Material exchange (X)

Isolated system
Energy exchange (X)
Material exchange (X)

Internal energy of a reaction system (*E*)

Kinetic Energy: the energy of *motion* (**translation**, **vibration** and **rotation**).

- Depends on 1) the **mass** of the particle
  2) the **speed** of the particle
  3) **temperature**

$E_K = 1/2\ mv^2$

Potential Energy: the energy of ***interaction*** between particles

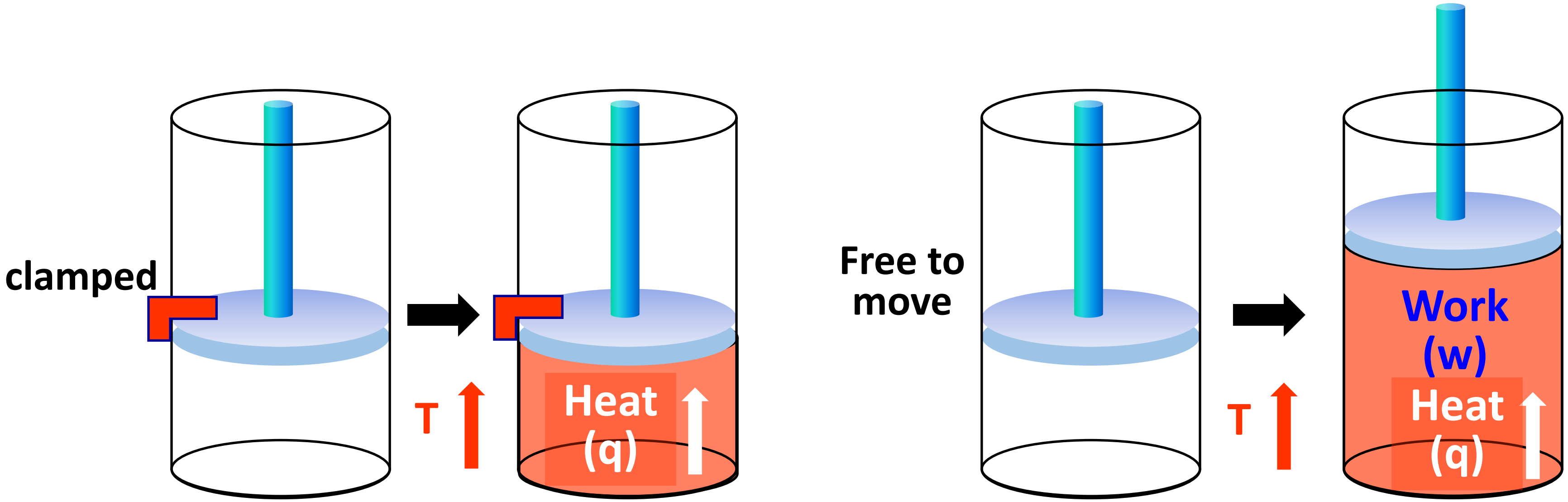
- The energy that comes from their ***stickiness***.
- Depend on 1) **Distance** between particles
  2) **Charge**-**Coulomb** force
  3) **Dipole moment-** e.g) Hydrogen bonding
  4) **Number of electrons**-London dispersion force
  5) **Covalent or noncovalent bonding** energy

Total internal energy = K.E. + P.E. + $E_{electrons}$ + $E_{nucleus}$

Internal energy, work and heat

Energy is the capacity to:

1. **to transfer heat** within the inside or towards outside of the system
2. **to do work** for the inside or outside of the system



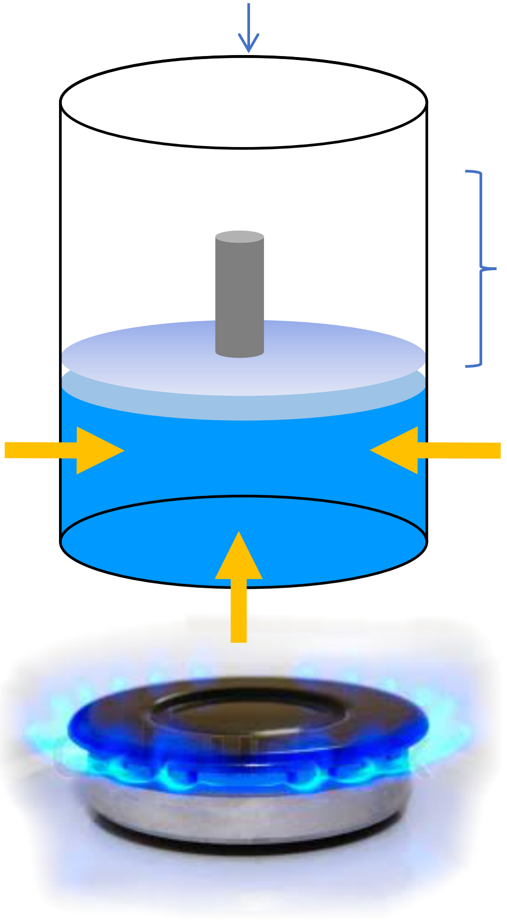
Energy in system	$\Delta E_{\text{system}} = q$	$\Delta E_{\text{system}} = q + w$
Molecular Motion	Random ↑	Random↑ + coherent/directional↑
Temperature	↑	↑

Internal energy, work and heat for a “system”

$$\Delta E = q + w$$

The change in internal energy within a system is converted to heat or work
(another way to state the first law of thermodynamics).

P_{ext}:constant



Work done to surroundings
System energy decrease

$$w = -P_{ext}\Delta V \leftarrow$$

Volume change

Heat absorbed

$$q > 0$$

$$\Delta E = q_p - P_{ext}\Delta V$$

const. pressure

$$\Leftrightarrow \quad q_p = \Delta E + P_{ext}\Delta V$$

Definition of enthalpy (H):

Energy released upon reaction
in the form of “HEAT” (measurable) at constant pressure

$$H = E + PV$$

Internal energy Pressure Volume

All types of energy related to bonding and movement
of particles (rotation, vibration and translation):

For the changes in energies upon reaction at constant pressure,

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

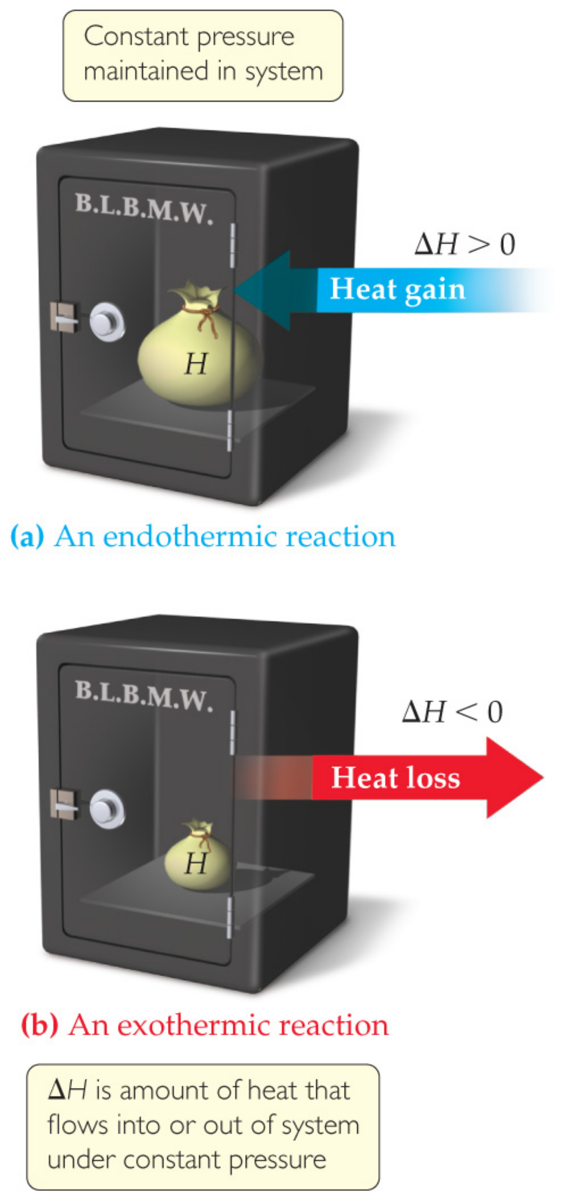
Since $\Delta E = q + w$ (the first law of thermodynamics) and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

“At *constant P*, the change in **enthalpy** *is* the **heat** gained or lost.”

Endothermic and Exothermic



(a) An endothermic reaction

(b) An exothermic reaction

- A process is endothermic when ΔH is positive.
- A process is exothermic when ΔH is negative.

Enthalpy of Reaction

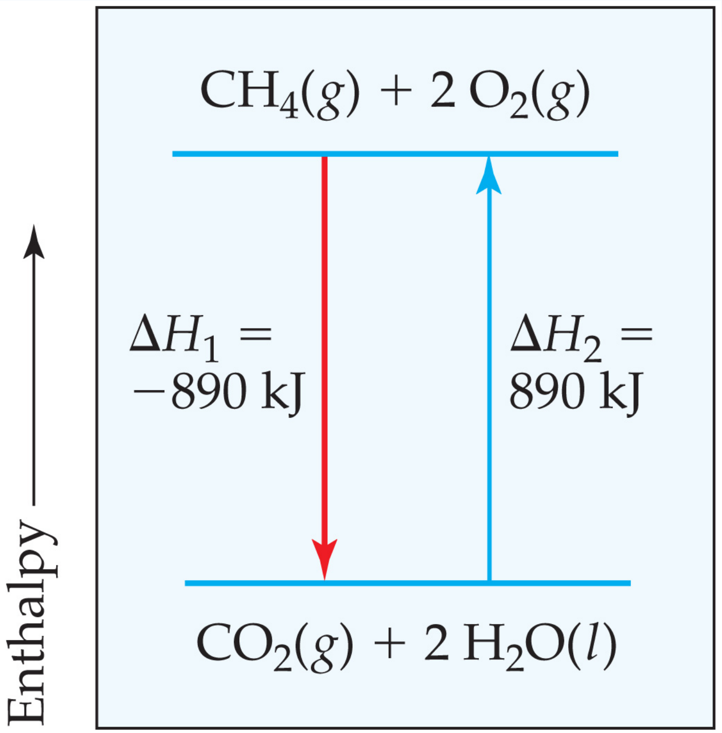
The *change* in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:

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

- Enthalpy is an extensive property.
- ΔH for a forward reaction is equal in size, but opposite to ΔH for the reverse reaction.

(If the enthalpy change is ΔH for R → P,

it is $-\Delta H$ for P → R)



Heat Capacity and Specific Heat

Heat capacity (or molar heat capacity)

- The amount of energy required to raise the temperature of a substance by 1 K (1 °C) is its **heat capacity**, usually given for one mole of the substance.
- Unit: J/K/mol

Specific heat capacity (or simply specific heat)

- The amount of energy required to raise the temperature of 1 g of a substance by 1 K (or 1 °C).
- Unit: J/K/g

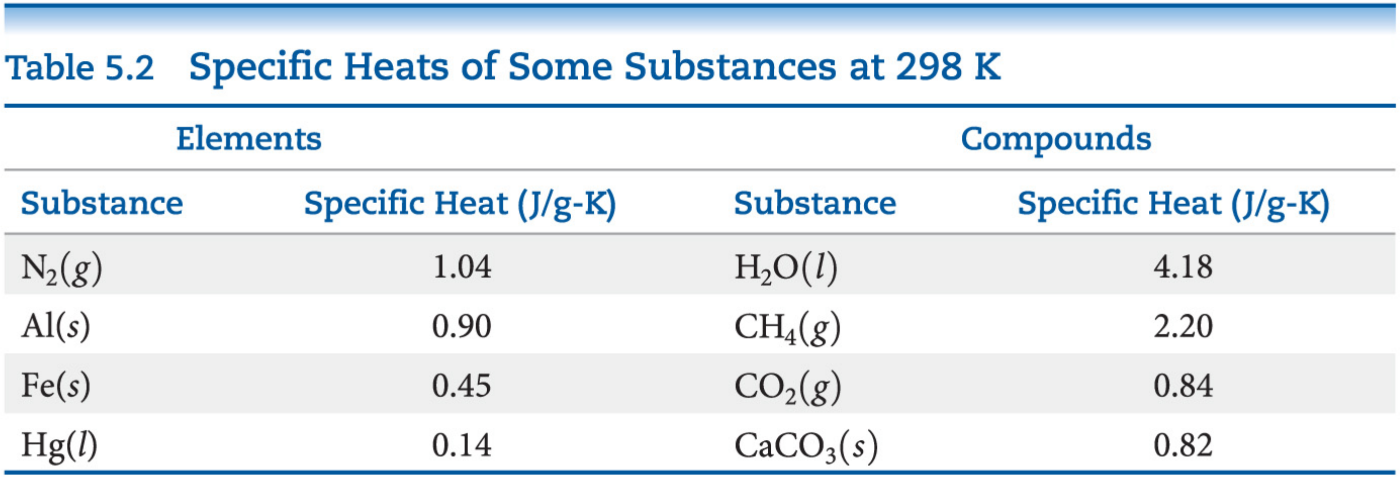


Table 5.2 Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	Specific Heat (J/g-K)	Substance	Specific Heat (J/g-K)
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

Heat Capacity and Specific Heat

$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

$$C_s = \frac{q}{m \times \Delta T}$$

Heat capacity is defined either at constant pressure or constant volume.

State Functions

- The quantity of a system, which is independent of the path by which the system achieved that state.

- These quantities include internal energy (*E*), enthalpy (*H*), entropy (*S*), free energy (*G*), etc.

- These quantities are uniquely defined under a given set of condition (temperature, pressure, volume, pH, solvent composition, etc.).

- **The changes in these quantities depends only on their initial and final quantities.**

For example, $\Delta E = E_{\text{final}} - E_{\text{initial}}$

Hess' Law

"The heat of a chemical reaction (that is, its ENTHALPY CHANGE) is INDEPENDENT of the route taken to convert the reactants into the products"

If we can divide a chemical reaction into a sum of many separate chemical reactions, then the SUM of all the separate enthalpy changes for each reaction is equal to the enthalpy change of the total reaction.

Suppose we already studied these two reactions:

1) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -394 \text{ kJ}$

2) $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -283 \text{ kJ}$

Then show that we know Δ*H* of this one without doing more experiments:

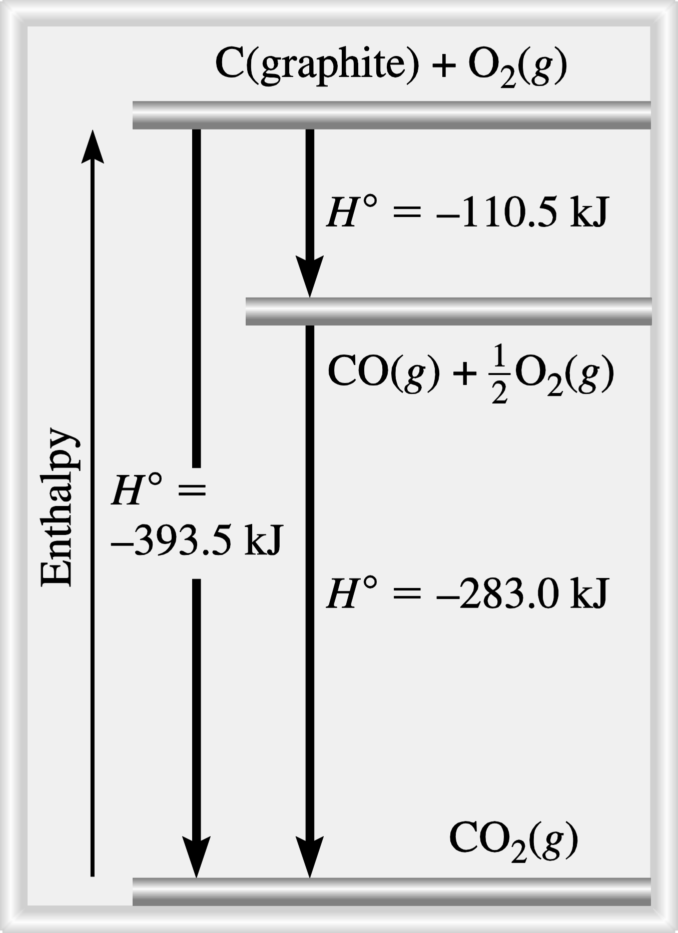
$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H = ?$$

Hess' Law

1) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -394\ \text{kJ}$

2) $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -283\ \text{kJ}$

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H = ?$$



ADD REACTION 1 to INVERSE REACTION 2:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -394\ \text{kJ}$$

+

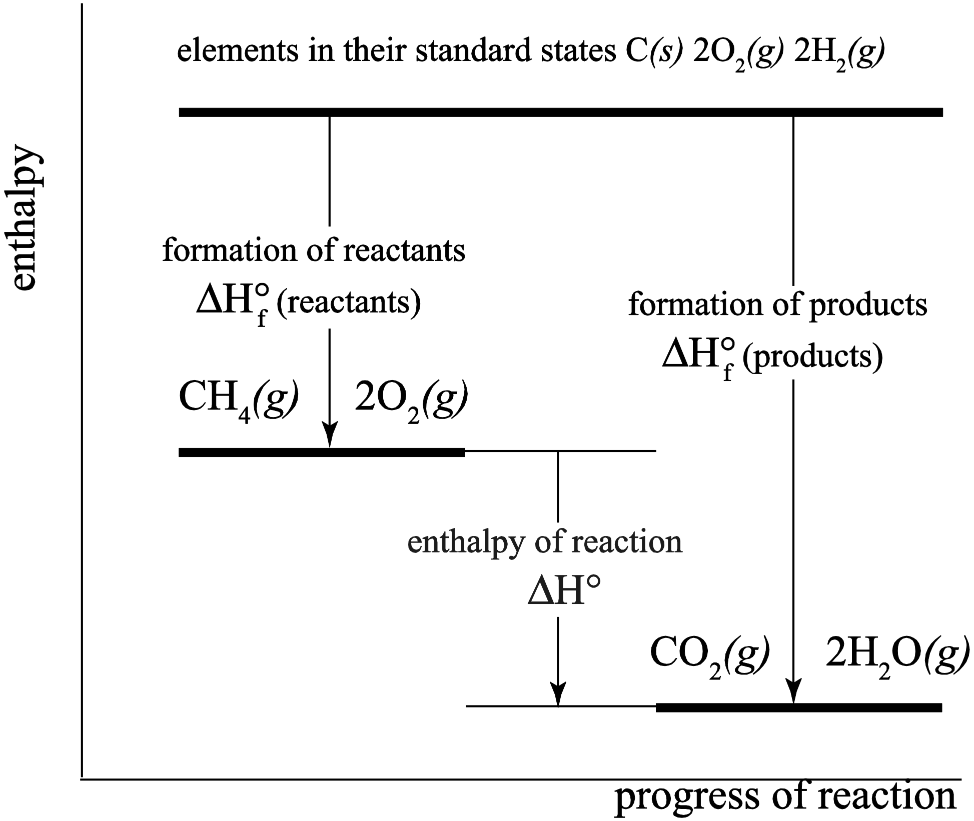
$$CO_{2(g)} \longrightarrow CO_{(g)} + \frac{1}{2}O_{2(g)} \qquad \Delta H = +283\ \text{kJ}$$

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H = -111\ \text{kJ}$$

Remember that inverting a reaction also INVERTS the sign of its enthalpy change:

That is, if energy is released to go one way, then it must be absorbed to go in the opposite direction!

Hess' Law



By definition,

Enthalpy of "elements" in their standard states = 0

$$\Delta H^{o}_{reaction} = \sum \Delta H^{o}_{f}(\text{products}) - \Delta H^{o}_{f}(\text{reactants})$$

What's missing in everything we've said?

Stuff get's made…..
By some mechanism…. series of events

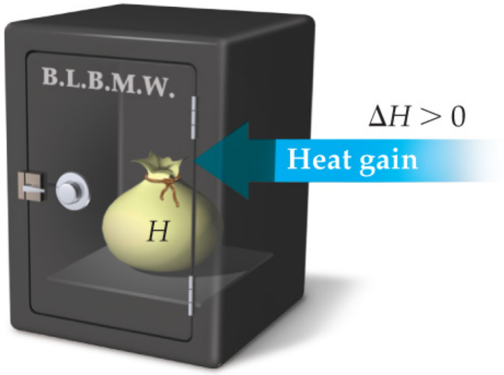
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -394\ \text{kJ}$$

$$+\quad CO_{2(g)} \longrightarrow CO_{(g)} + \frac{1}{2}O_{2(g)} \qquad \Delta H = +283\ \text{kJ}$$

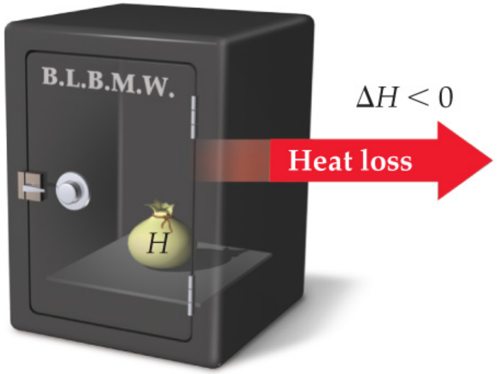
$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H = -111\ \text{kJ}$$

Energy goes in or out

Constant pressure maintained in system



(a) An endothermic reaction



(b) An exothermic reaction

ΔH is amount of heat that flows into or out of system under constant pressure

What’s missing in everything we’ve said?

Stuff get’s made…..

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -394\ \text{kJ}$$

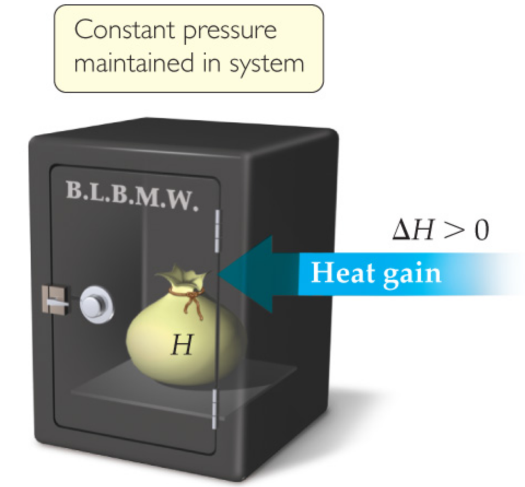
$$+$$

$$CO_{2(g)} \longrightarrow CO_{(g)} + \frac{1}{2}O_{2(g)} \qquad \Delta H = +283\ \text{kJ}$$

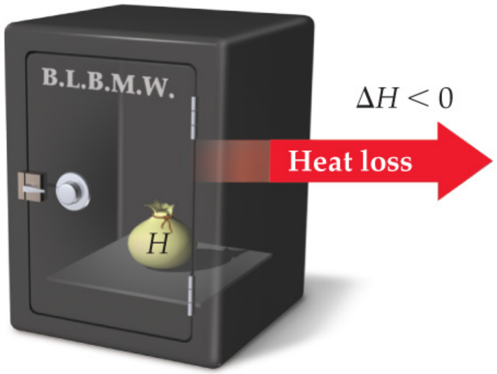
$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H = -111\ \text{kJ}$$

- **We’ve got *what***
  - **Reactants become products)**
  - **Energy in or out**
- **We’ve got *how***
  - **a reaction mechanism,**
  - **speed, kinetics.**
- **But *Why?……***

Energy goes in or out



(a) An endothermic reaction

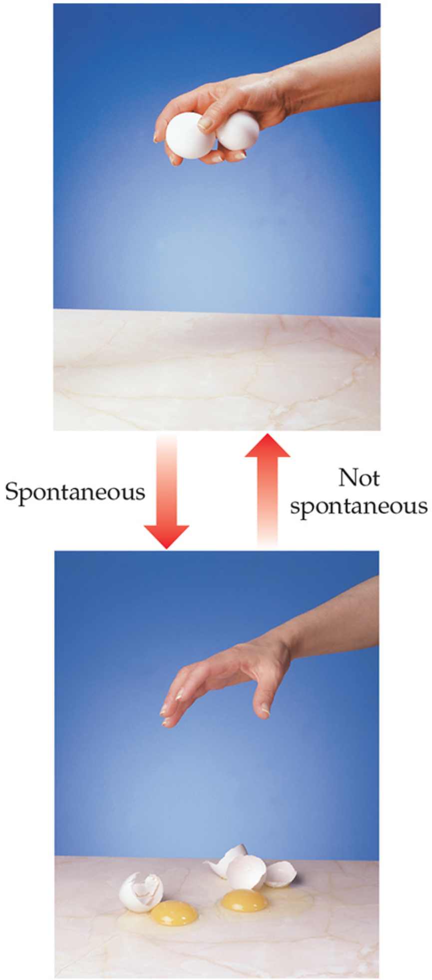


(b) An exothermic reaction

ΔH is amount of heat that flows into or out of system under constant pressure

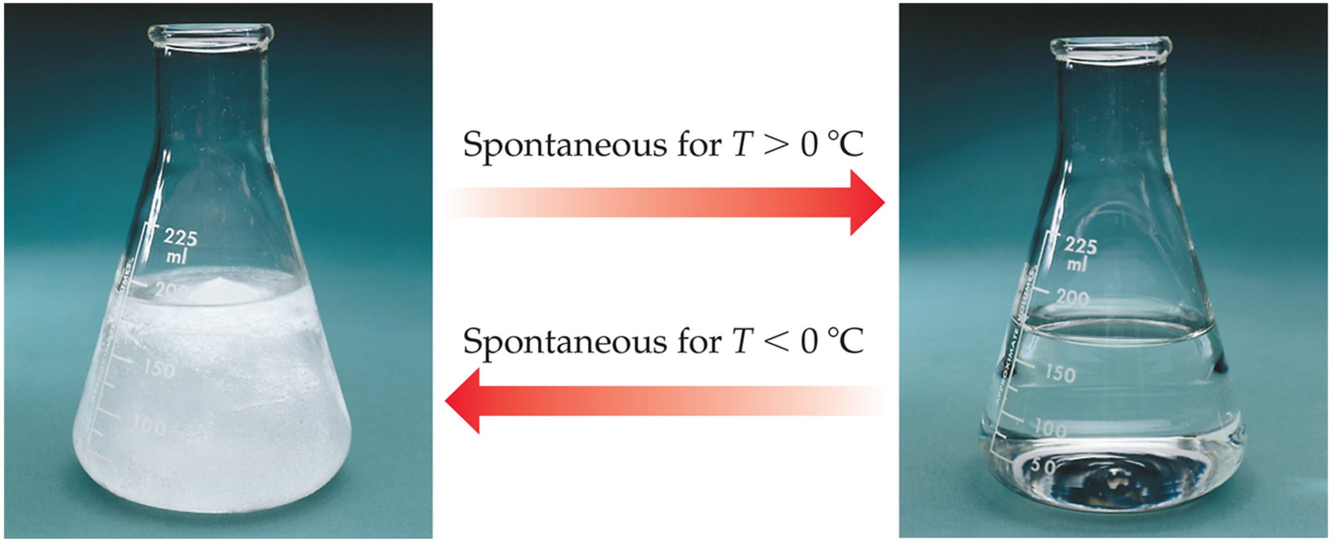
What’s missing in everything we’ve said?

- **We’ve got *what***
  - **Reactants become products)**
  - **Energy in or out**
- **We’ve got *how***
  - **a reaction mechanism,**
  - **speed, kinetics.**
- **But *Why?......***
- ***Spontaneous means it happens.***
- ***Nonspontaneous means it won’t***

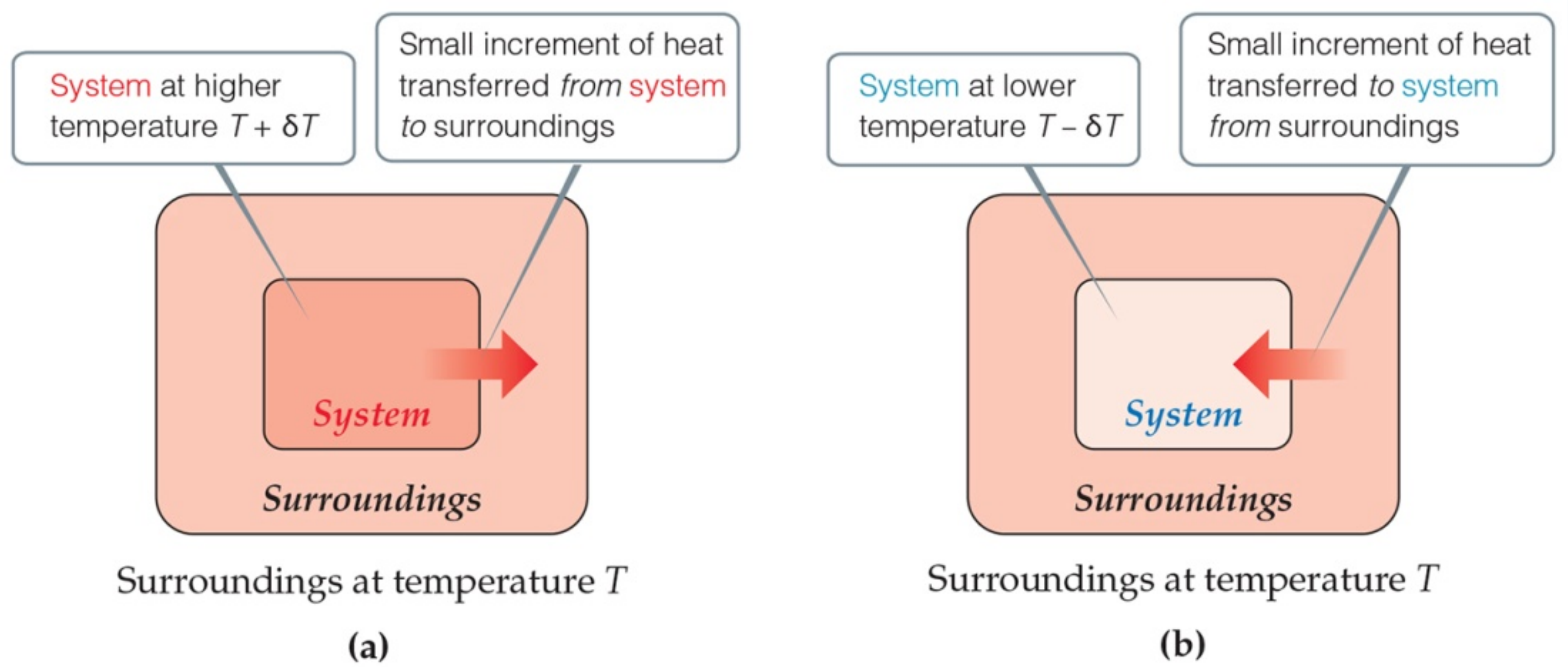


Conditions clearly matter….

- Temperature and pressure can affect spontaneity.
- Spontaneousness defined by:
  - The **stuff**
  - The **conditions** the stuff is in.



To Figure out the why…..
We've got to think about the process a bit more.



Surroundings at temperature T

(a)

Surroundings at temperature T

(b)

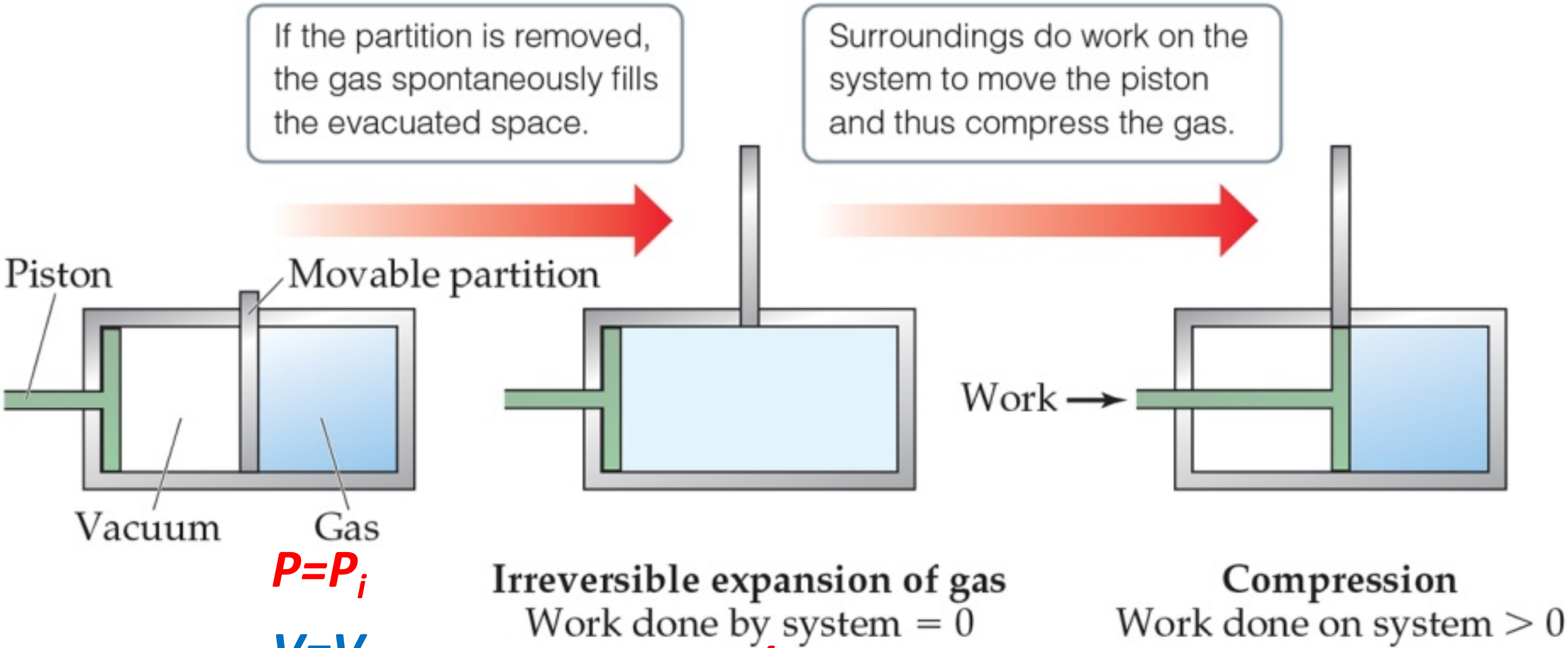
Reversible process: A very special kind of process:

The process can be *exactly* reversed

It can go in exactly the opposite direction.

But that's weird…. That kind of process doesn't have a single direction.

Reversible and Irreversible Processes



If the partition is removed, the gas spontaneously fills the evacuated space.

Surroundings do work on the system to move the piston and thus compress the gas.

Irreversible expansion of gas
Work done by system = 0

Compression
Work done on system > 0

$P = P_i$

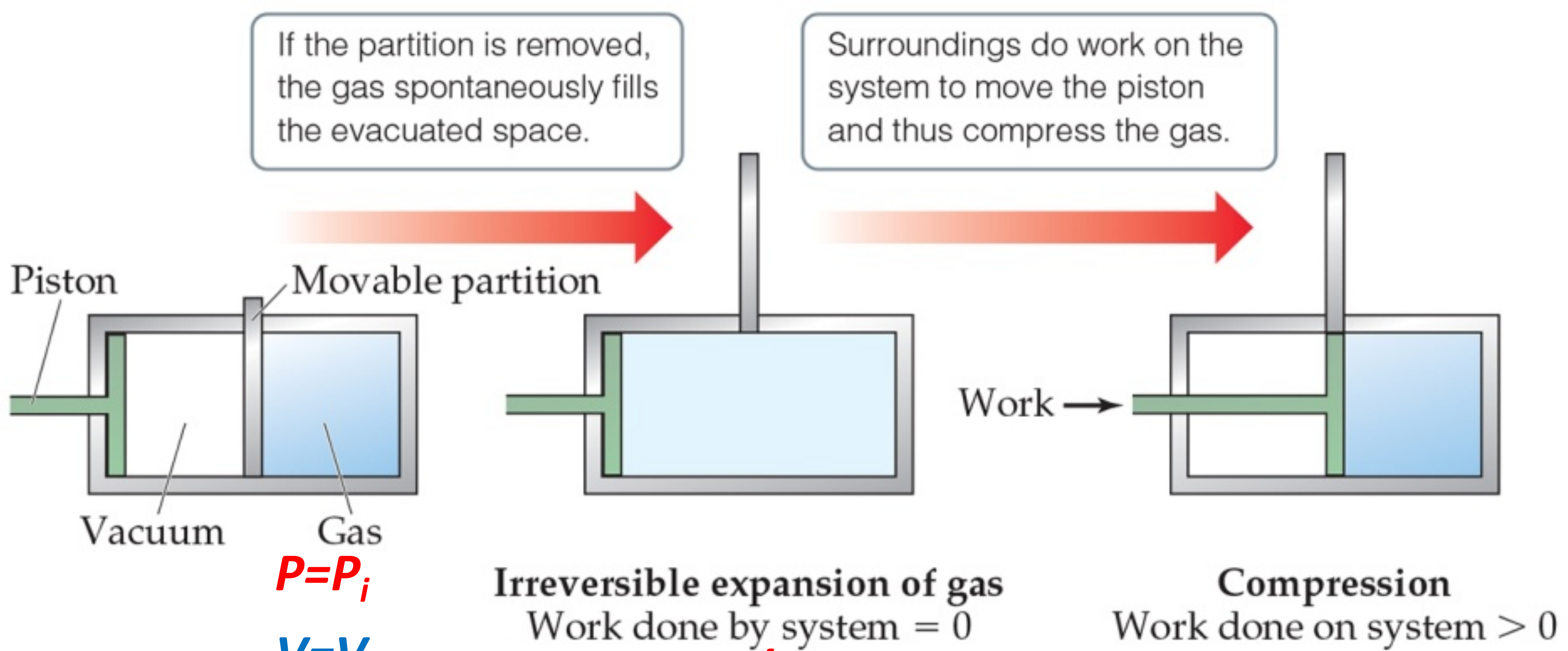
$V = V_i$

$P = 1/2 P_i$

$V = 2V_i$

- ***Why can't you go back spontaneously?***

Reversible and Irreversible Processes



$P=P_i$

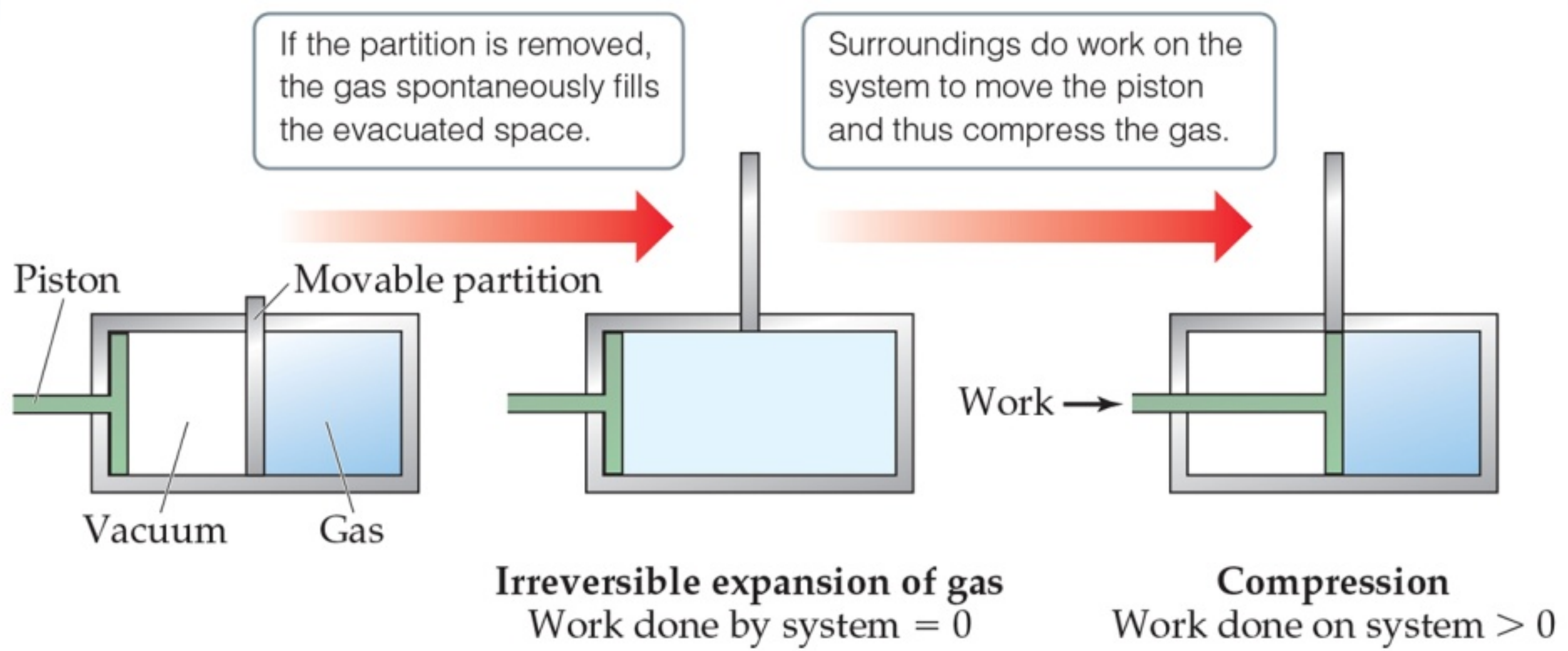
$V=V_i$

$P=1/2P_i$

$V=2V_i$

- *Why can't you go back spontaneously?*
- *What are the odds?*
    - *All the gas molecules swimming back to one side of the container.*

Reversible and Irreversible Processes



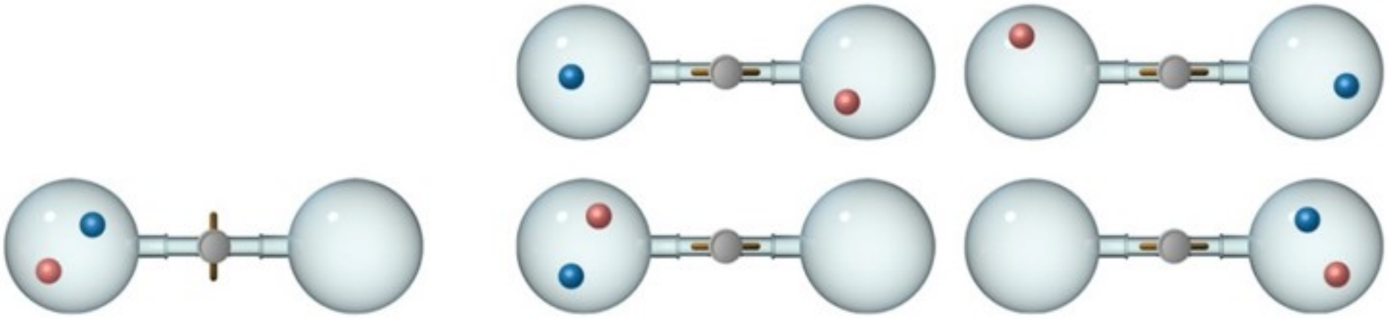
Irreversible expansion of gas
Work done by system = 0

Compression
Work done on system > 0

- **Irreversible processes:** cannot be undone by ***exactly*** reversing the change.
- Because spontaneous process are ***real*** processes,
- ***all spontaneous processes are irreversible.***

What is Entropy?
Entropy is a measure of randomness.

- Consider the expansion of only **two** gas molecules.
- Originally confined to the left flask. Open the stopcock.



(a) The two molecules are colored red and blue to keep track of them.

(b) Four possible arrangements (microstates) once the stopcock is opened.

- The probability they both return to the left flask? $\left(\frac{1}{2}\right)^2$
- If one mole of gas molecules are used? $\left(\frac{1}{2}\right)^{6.02\times10^{23}}$!(**Zero**!)
  - Zero likelihood that all gas molecules will be in the left flask at the same time.

Entropy and the Second Law of Thermodynamics

- **Entropy** (randomness) is a state function:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

- It is related to heat transfer between surroundings and system:

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (\text{constant } T)$$

Second Law of Thermodynamics

- The **entropy** of the **universe** increases in any spontaneous process.
- Spontaneous process: any process that has a single **direction.**
- This results in the following relationships:

$$\textbf{Reversible Process:}\quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

$$\textbf{Irreversible Process:}\quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- We now have our reason for the direction of any process.
- The universe always becomes more random.
- But why?
- There is a very good reason.

Because it's made up of many many tiny things. (atoms molecules) Boltzman Equation and Microstates

- **Statistical thermodynamics**
  - Explains bulk behavior
  - By relating it to the microscopic behavior of molecules/atoms.
- **Microstate:**
  - One possible arrangement of position and kinetic energy of molecules
    - ***That will result in the bulk condition!!!***
      - ***T, V, P, n, electric field, etc.***
  - Many molecules, many microstates.
    - Odds of any one of them essentially zero.
  - *Let W* represent the total number of **possible** microstates:
  - The connection between the number of microstates and the entropy of the system ***in a given state*** is the Boltzman Equation:

$$S = k \ln W$$

Entropy Change

- Since entropy is a state function, the final value minus the initial value will give the overall change.
- The change in entropy when we go form one **state** to another.
- Different states results in a different number of possible microstates (more or less disorder).

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$

- ***Entropy increases when the number of microstates of a system increases.***

Statistical Definition of Entropy

ENTROPY is a measure of the number of different ways energy can be distributed.

Ludwig Boltzmann
1844-1906

"Boltzmann Equation"

$$\boxed{S = k \ln W}$$

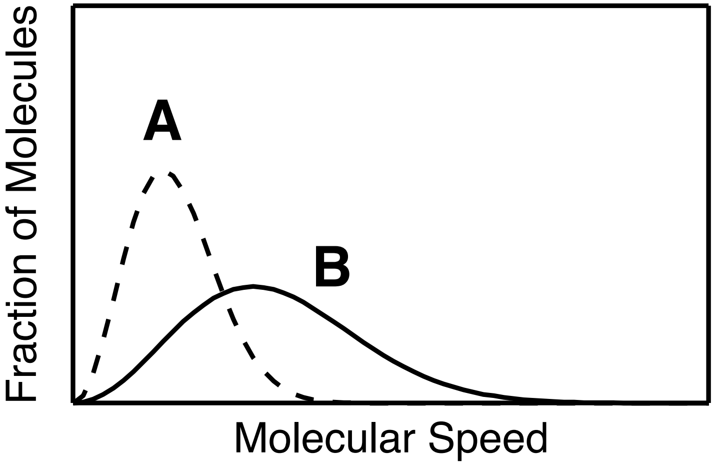
W : # of arrangements (degeneracy), or "microstates"

k : Boltzmann Constant

N_A: Avogadro's number

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$$

What is the unit of entropy? **J·K^{-1}**



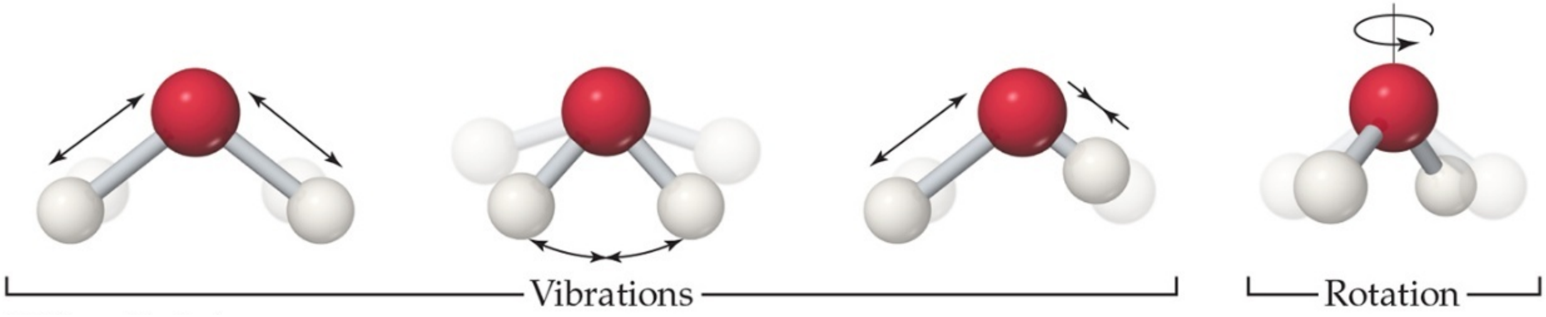
These curves are called Boltzmann distributions.

Which state has a large entropy (A or B)?

The broader peak means the larger Entropy

Molecular Motions and Energy

- Molecules exhibit several types of motion (degrees of freedom).
  - **Translational**: Movement of the entire molecule from one place to another.
  - **Vibrational**: Periodic motion of atoms within a molecule.
  - **Rotational**: Rotation of the molecule about an axis.



- **These are included in the number of a system's microstates.**

Microstates: Volume, Temperature and Number of Atoms affect Entropy

- The number of microstates possible for a system increases with
  - an increase in **volume** (more possible positions).
  - an increase in **temperature** (greater distribution of molecular speed).
  - an increase in the **number** of **atoms/molecules** (more degrees of freedom).
- Each factor increases entropy—the randomness or disorder of the system.

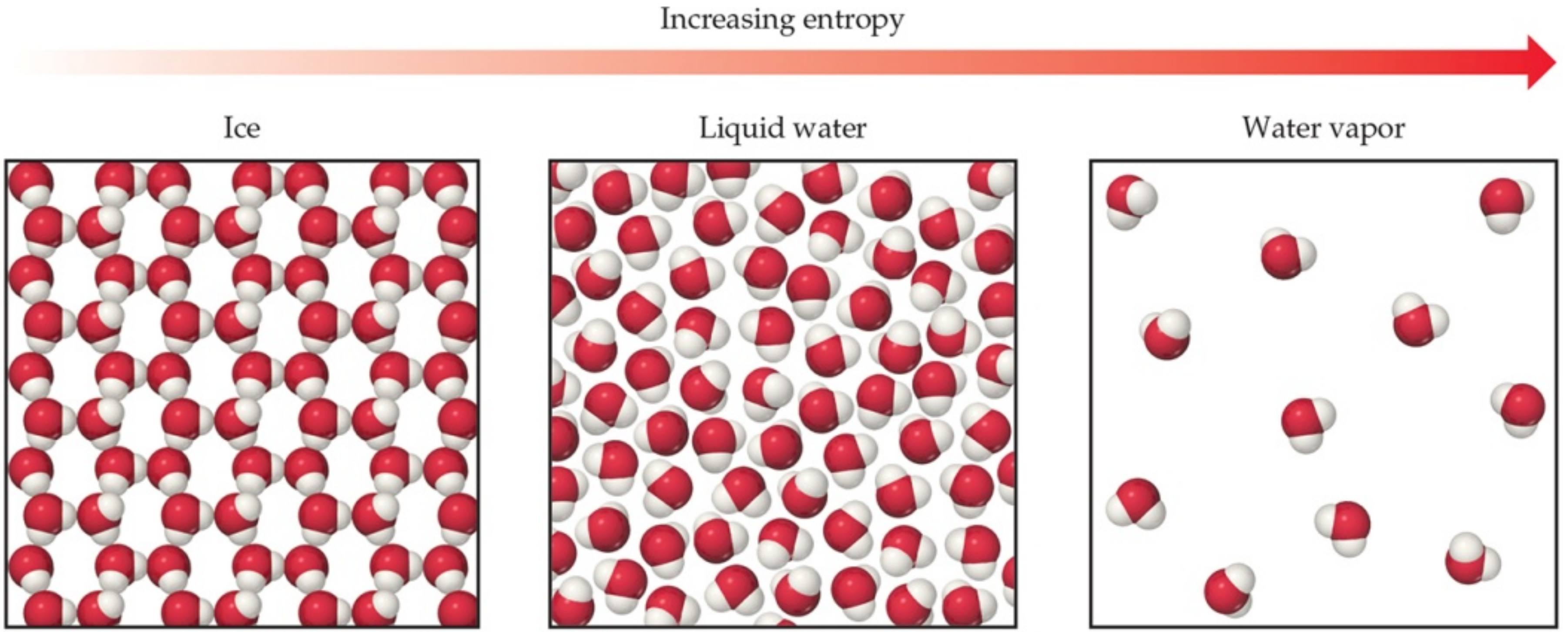
Entropy and Physical State (solid/gas/liquid)

- Entropy **increases** with the **freedom of motion** of molecules.

- $S(g) > S(l) > S(s)$

- Entropy of a system increases when:
  - **gases form** from either solids or liquids.
  - **liquids or solutions** form from solids.
  - the number of **gas molecules increases** during a chemical reaction.

Entropy and Physical States



Ice

Rigid, crystalline structure

Motion restricted to **vibration** only

Smallest number of microstates

Liquid water

Increased freedom with respect to **translation**

Free to **vibrate** and **rotate**

Larger number of microstates

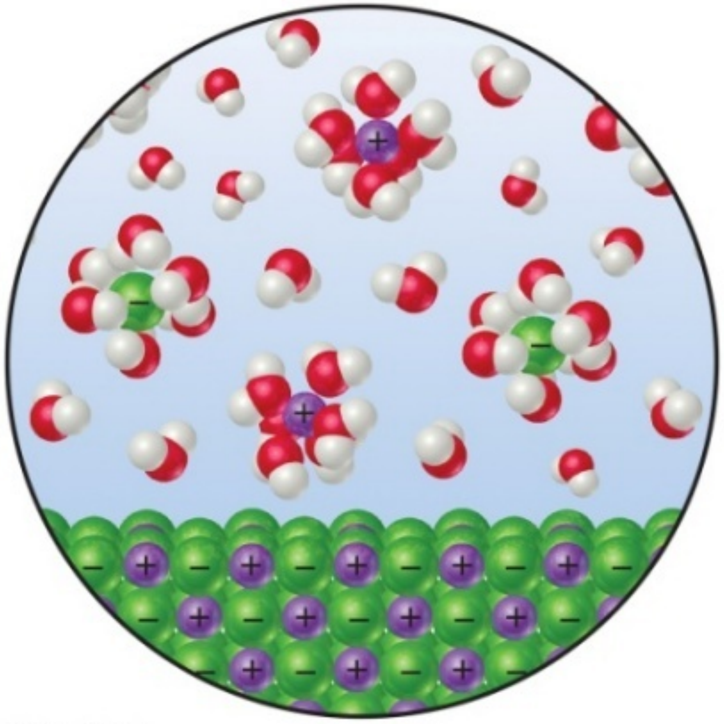
Water vapor

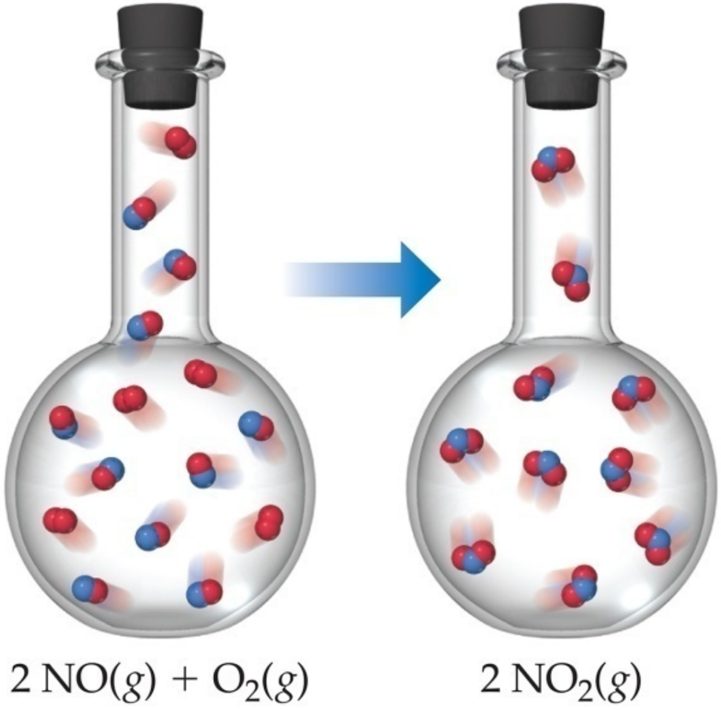
Molecules spread out, essentially independent of one another

Complete freedom for **translation**, **vibration**, and **rotation**

Largest number of microstates

More or less entropy?





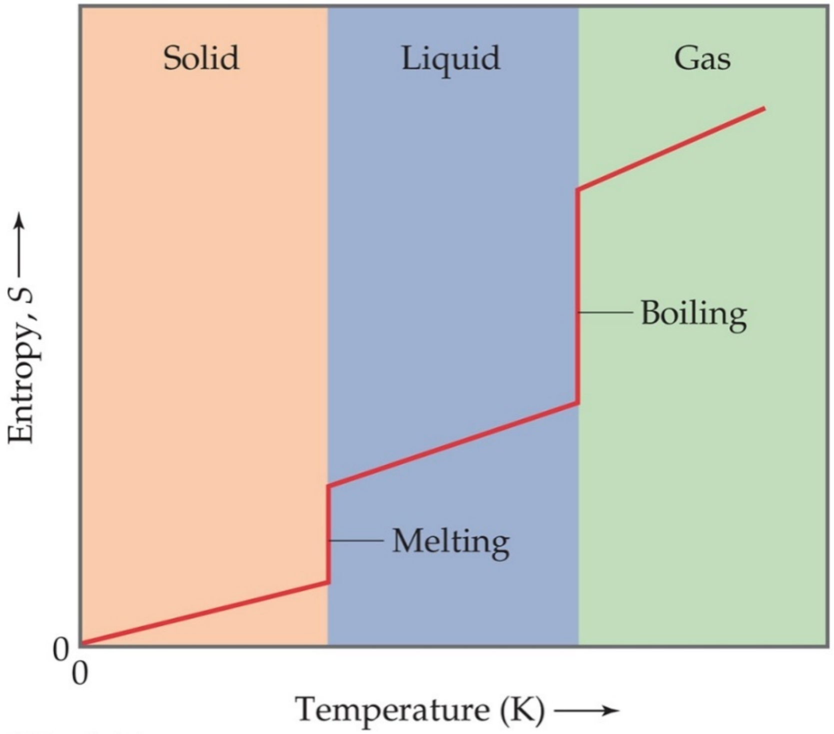
Third Law of Thermodynamics

- The entropy of a pure crystalline substance at absolute zero is 0.
- Consider all atoms or molecules in the perfect lattice at 0 K; there will only be **one** microstate.

$$S = k \ln W$$

$$W = 1 \quad \ln(1) = 0$$

$$S = k \ \ln(1) = 0$$



19.4 Entropy Changes in Chemical Reactions

Since Entropy is a State function, Just like Enthalpy (H)

You can calculate ΔS for a reaction in a similar way:

$$\Delta S^\circ = \Sigma n \Delta S^\circ(\text{products}) - \Sigma m \Delta S^\circ(\text{reactants})$$

ΔS^0 Is the Standard molar change in Entropy.

n and *m* coefficients of the balanced chemical equation.

- ΔS^0
  - is ***not zero*** for the **elements** in their standard state.
  - values of $(\mathrm{g}) > (\mathrm{l}) > (\mathrm{s})$
  - **increases** with mo**lar mass** and number of **atoms**

Standard Molar Entropies

Substance	$S°(\text{J/mol}\cdot\text{K})$
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Table 19.1 Standard Molar Entropies of Selected Substances **at 298 K**

Calculating $\Delta S°$ from Tabulated Entropies

Calculate the change in the standard entropy of the system, $\Delta S°$, for the synthesis of ammonia from $N_2(g)$ and $H_2(g)$ at 298 K:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Solution

Analyze We are asked to calculate the standard entropy change for the synthesis of $NH_3(g)$ from its constituent elements.

Plan We can make this calculation using Equation 19.8 and the standard molar entropy values in **Table 19.1** and Appendix C.

Table 19.1 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$(J/mol – K)
$H_2(g)$	130.7
$N_2(g)$	191.6
$O_2(g)$	205.2
$H_2O(g)$	188.8
$NH_3(g)$	192.8
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9
$CH_3OH(l)$	127.2
$C_6H_6(l)$	173.3

Table 19.1 [continued]

Substance	$\mathbf{S^\circ (J/mol-K)}$
$Li(s)$	29.1
$Na(s)$	51.3
$K(s)$	64.7
$Fe(s)$	27.3
$FeCl_3(s)$	142.2
$NaCl(s)$	72.1

Solve

Using Equation 19.8, we have:

$$\Delta S^\circ = 2\ S^\circ(NH_3) - [S^\circ(N_2) + 3\ S^\circ(H_2)]$$

$\Delta S°$

$$N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$$

Substituting the appropriate $S°$ values from **Table 19.1** yields:

$$\Delta S° = 2\ S°(NH_3) - \left[S°(N_2) + 3\ S°(H_2)\right]$$

$$\Delta S° = (2\ \cancel{mol})(192.8\ J/\cancel{mol}\text{-}K) - [(1\ \cancel{mol})(191.6\ J/\cancel{mol}\text{-}K)$$

$$+ (3\ \cancel{mol})(130.7\ J/\cancel{mol}\text{-}K)]$$

$$= -198.1\ J/K$$

Check The value for $\Delta S°$ is negative, in agreement with our qualitative prediction based on the decrease in the number of molecules of gas during the reaction.

Measuring Entropy in the bulk.

2nd LAW of THERMODYNAMICS

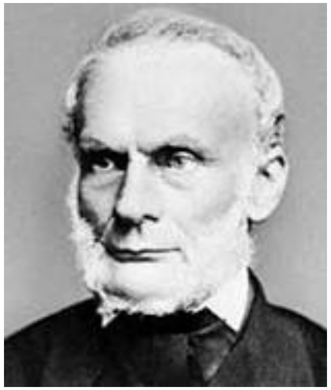
Spontaneous processes are those where the energy "dispersal" of the universe increases, *or "the ENTROPY of the universe always increases"*

How do we measure ENTROPY?

"Clausius Equation"

$$\boxed{\Delta S = \frac{q_{rev}}{T}}$$

Note:
Heat is ***disordered motion***,
work is ***uniform motion***.
Thus, this equation tells us that "**heat**" measures "**disorder**".



Rudolf Clausius
1822-1888

The ENTROPY CHANGE is the energy transferred as HEAT during a REVERSIBLE PROCESS, DIVIDED by the TEMPERATURE during that process.

*Dividing by T means that the entropy generated from heat is **large** when **T is small!** That is, dividing by T means the scaling of heat dispersal using temperature.*

Predicting Spontaneity Requires knowing ΔS of both ***system*** and ***surroundings*** ***But how do we know about the surrounding?***

- The ΔS of surroundings is due **only** to heat flow from system!
- For an isothermal process $$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-q_{\text{sys}}}{T}$$
- At constant pressure, q_{sys} is simply $\Delta H°$ for the system.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}\left[\text{at constant P}\right]$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

For spontaneous processes, $\Delta S_{\text{universe}} > 0$

We can predict direction using only Measurements of the *system.*

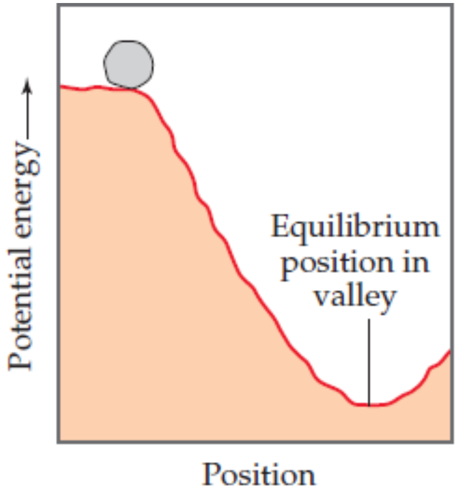
- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- Substitute for the entropy of the surroundings: $\Delta S_{\text{surr}} = \dfrac{-\Delta H_{\text{sys}}}{T}$ [at constant P]
  - $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \dfrac{\Delta H_{\text{system}}}{T}$
- Multiply by $-T$:
  - $-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$
- Rearrange:
  - $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$
- Call $-\boldsymbol{T\Delta S_{\text{universe}}}$ the **Gibbs Free Energy** (ΔG):
  - $$\Delta G = \Delta H - T\Delta S$$

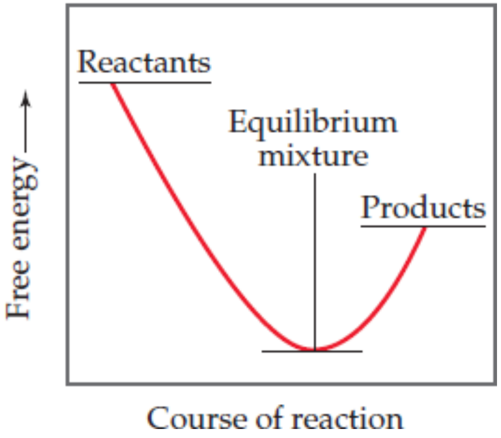
19.5 Gibbs Free Energy

- The fate of any process can be predicted
- Only three things are relevant:
    - Enthalpy of system
    - Temperature of system
    - ***Entropy of system***

ΔG, Gibbs Free Energy.

- A reaction going toward equilibrium…
- Is like a boulder rolling down a hill
- For the boulder the ”hill” is potential energy
- For the reaction the “hill” is Gibbs free energy.

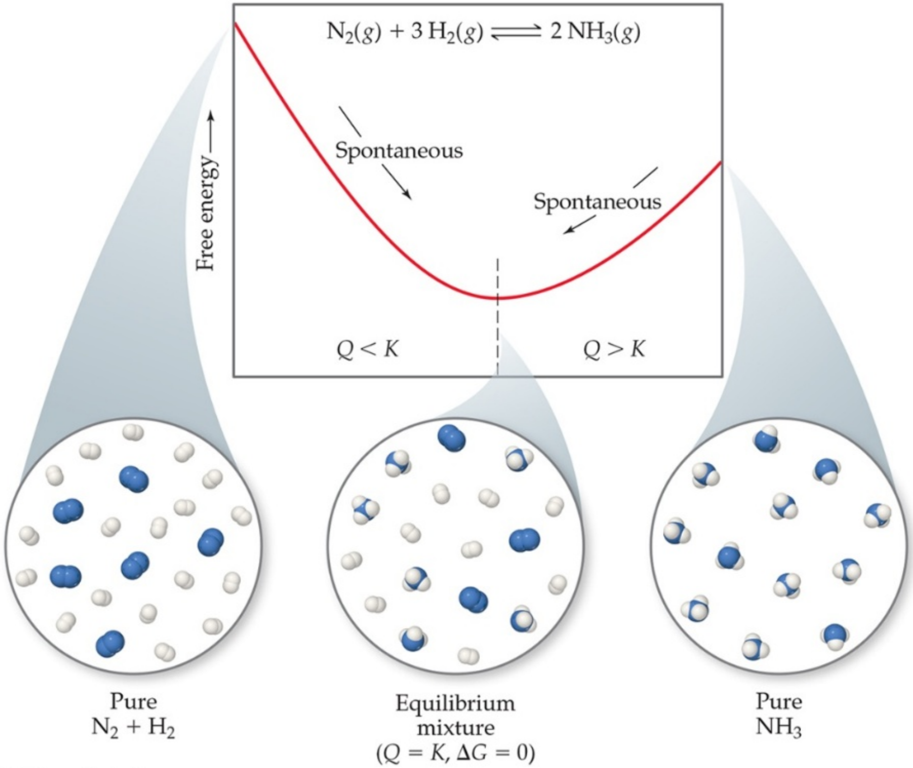




Gibbs Free Energy decides the fate of all processes

1) If ΔG is negative:
    1) $\Delta S^{univ.}$ Is positive
    2) Reaction moves forward.

2) If ΔG is zero:
    1) $\Delta S^{univ.}$ is zero
    2) Reaction at equilibrium
3) If ΔG is positive:
    1) ΔS^{univ} is negative
    2) Reaction moves backward.



Standard Free Energy of Formation (1 of 2)

Analogous to standard enthalpies of formation are standard free energies of formation, $\Delta G_f\,°$:

$$\Delta G° = \sum n\Delta G_f\,°(\text{products}) - \sum m\Delta G_f\,°(\text{reactants})$$

where *n* and *m* are the stoichiometric coefficients.

Standard Free Energy of Formation (2 of 2)

Table 19.2 Conventions Used in Establishing Standard Free Energies

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	1 atm pressure
Solution	1 *M* concentration
Element	$\Delta G_f^\circ = 0$ for element in standard state

Sample Exercise Calculating Standard Free-Energy Change from Free Energies of Formation (1 of 3)

(**a**) Use data from Appendix C to calculate the standard free-energy change for the reaction $P_4(g) + 6\ Cl_2(g) \longrightarrow 4\ PCl_3(g)$ at 298 K. (**b**)What is $\Delta G°$ for the ***reverse*** of this reaction?

Solution

Analyze We are asked to calculate the free-energy change for a reaction and then to determine the free-energy change for the reverse reaction.

Plan We look up the free-energy values for the products and reactants and use Equation 19.14. We multiply the molar quantities by the coefficients in the balanced equation and subtract the total for the reactants from that for the products.

Sample Exercise Calculating Standard Free-Energy Change from Free Energies of Formation (2 of 3)

Solve $P_4(g) + 6\ Cl_2(g) \longrightarrow 4\ PCl_3(g)$

(a) $Cl_2(g)$ is in its standard state, so ΔG_f° is zero for this reactant. $P_4(g)$, however, is not in its standard state, so ΔG_f° is not zero for this reactant. From the balanced equation and values from Appendix C, we have

$$\begin{aligned}\Delta G_{rxn}^\circ &= 4\Delta G_f^\circ[PCl_3(g)] - \Delta G_f^\circ[P_4(g)] - 6\Delta G_f^\circ[Cl_2(g)] \\ &= (4\ \cancel{mol})(-269.6\ kJ/\cancel{mol}) - (1\ \cancel{mol})(24.4\ kJ/\cancel{mol}) - 0 \\ &= -1102.8\ kJ\end{aligned}$$

ΔG° is negative, so a mixture of $P_4(g)$, $Cl_2(g)$, and $PCl_3(g)$ at 25°C, each present at a partial pressure of 1 atm, should react spontaneously in the forward direction to form more PCl_3.

Sample Exercise Calculating Standard Free-Energy Change from Free Energies of Formation (3 of 3)

Remember, however, that the value of ΔG° tells us nothing about the rate at which the reaction occurs.

(**b**) When we reverse the reaction, we reverse the roles of the reactants and products. Thus, reversing the reaction changes the sign of ΔG in Equation 19.14, just as reversing the reaction changes the sign of ΔH. (Section 5.4) Hence, using the result from part (a), we have

$$4\ \mathrm{PCl_3}(g) \longrightarrow \mathrm{P_4}(g) + 6\ \mathrm{Cl_2}(g) \qquad \Delta G^\circ = +1102.8\ \mathrm{kJ}$$

Practice Exercise

Use data from Appendix C to ΔG° at 298 K for the combustion of methane:

$$\mathrm{CH_4}(g) + 2\ \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\ \mathrm{H_2O}(g)$$

19.6 Free Energy and Temperature (1 of 2)

- **Tabulations** of Standard Free Energy of Formation only allow for calculations at 298 K (25 °C).
- To look at other temperatures, we'll need to use the equation:

$$\Delta G = \Delta H - T\Delta S$$

- Since reactions are spontaneous when $\Delta G < 0$, the signs and magnitude of enthalpy and entropy and the value of temperature can be used to calculate ΔG and determine spontaneity.

19.6 Free Energy and Temperature (2 of 2)

Table 19.3 How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	**Reaction Characteristics**	**Example**
$-$	$+$	$-$	$-$	Spontaneous at all temperatures	$2\ O_3(g) \rightarrow 3\ O_2(g)$
$+$	$-$	$+$	$+$	Nonspontaneous at all temperatures	$3\ O_2(g) \rightarrow 2\ O_3(g)$
$-$	$-$	$+$	$+$ or $-$	Spontaneous at low *T*; nonspontaneous at high *T*	$H_2O(l) \rightarrow H_2O(s)$
$+$	$+$	$-$	$+$ or $-$	Spontaneous at high *T*; nonspontaneous at low *T*	$H_2O(s) \rightarrow H_2O(l)$

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity (1 of 6)

The Haber process for the production of ammonia involves the equilibrium

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ )(g)$$

For this reaction, $\Delta H^\circ = -91.88\ \text{kJ}$ and $\Delta S^\circ = -198.1\ \text{J/K}$. Assume that ΔH° and ΔS° for this reaction do not change with temperature. (**a**) Predict the direction in which ΔG for the reaction changes with increasing temperature. (**b**) Calculate ΔG at 25 °C and at 500 °C.

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity (2 of 6)

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,)(g)$$

Plan We can answer part (a) by determining the sign of ΔS for the reaction and then using that information to analyze Equation 19.12. In part (b), we use the given ΔH° and ΔS° values for the reaction together with Equation 19.12 to calculate ΔG.

Solve

$$\Delta G = \Delta H - T\Delta S.$$

(**a**) The temperature dependence is only in the Entropy term if $\Delta \mathrm{H}$ and $\Delta \mathrm{S}$ stay constant. What do you think the sign of $\Delta \mathrm{S}$ will be?

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity (2 of 6)

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,)(g)$$

Plan We can answer part (a) by determining the sign of ΔS for the reaction and then using that information to analyze Equation 19.12. In part (b), we use the given ΔH° and ΔS° values for the reaction together with Equation 19.12 to calculate ΔG.

Solve

$$\Delta G = \Delta H - T\Delta S.$$

(a) The temperature dependence is only in the Entropy term if ΔH and ΔS stay constant. What do you think the sign of ΔS will be?

NEGATIVE! (fewer gas molecules in product)

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity (3 of 6)

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,)(g)$$

If ΔS is negative, $T\Delta S$ **has** to be positive.

Raising T, makes ΔG more positive.

Raising T drives the reaction toward ***reactants.***

(**b**) If we assume that the values for ΔH° and ΔS° do not change with temperature, we calculate ΔG at any temperature. At $T = 25^\circ\text{C} = 298\ \text{K}$, we have

$$\Delta G = \Delta H - T\Delta S.$$

$$\Delta G^\circ = -91.88\text{ kJ} - (298\,\cancel{\text{K}})(-198.1\,\cancel{\text{J}}\,/\,\cancel{\text{K}})\left(\frac{1\text{ kJ}}{1000\,\cancel{\text{J}}}\right)$$

$$= -91.88\text{ kJ} + 59.0\text{ kJ} = -32.8\text{ kJ}$$

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity (4 of 6)

At $T = 500°\text{C} = 773\text{K},$ we have

$$\Delta G = -91.88\text{ kJ} - (773\text{ K})(-198.1\,\cancel{\text{J}}\,/\,\cancel{\text{K}})\left(\frac{1\,\text{kJ}}{1000\,\cancel{\text{J}}}\right)$$

$$= -91.88\text{ kJ} + 153\text{ kJ} = 61\,\text{kJ}$$

Notice that we had to convert the units of $-T\Delta S°$ to kJ in both calculations so that this term can be added to the $\Delta H°$ term, which has units of kJ.

Comment Increasing the temperature from 298 K to 773 K changes ΔG from $-32.8\,\text{kJ}$ to $+61\text{kJ},$ where the result at 773 K assumes that $\Delta H°$ and $\Delta S°$ do not change with temperature. Although these values do change slightly with temperature, the result at 773 K should be a reasonable approximation.

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity (5 of 6)

The positive increase in ΔG with increasing *T* agrees with our prediction in part (a). Our result indicates that in a mixture of $N_2(g)$, $H_2(g)$, and $NH_3(g)$, each present at a partial pressure of 1 atm, the $N_2(g)$ and $H_2(g)$ react spontaneously at 298 K to form more $NH_3(g)$. At 773 K, the positive value of ΔG tells us that the reverse reaction is spontaneous. Thus, when the mixture of these gases, each at a partial pressure of 1 atm, is heated to 773 K, some of the $NH_3(g)$ spontaneously decomposes into $N_2(g)$ and $H_2(g)$.

Gibbs Free Energy

What is the meaning of the term "free" in Gibbs free energy?

(1st law) $\Delta E = q + w$

$$= T \cdot \Delta S + \overbrace{\left(\underbrace{w_{expansion}}_{-P\Delta V \text{ ("mechanical work")}} + \underbrace{w_{extra}}_{\text{Any types of work other than mechanical work (e.g., chemical reaction)}} \right)}^{\textit{all types of work}}$$

(Clausius equation)

$$w_{extra} = \Delta E_{Sys} - w_{expansion} - T\Delta S_{Sys}$$

$$w_{extra} = \Delta H_{Sys} - P\Delta V - w_{expansion} - T\Delta S_{Sys}$$

$$w_{extra} = \Delta H_{Sys} + w_{expansion} - w_{expansion} - T\Delta S_{Sys}$$

$$w_{extra} = \Delta H_{Sys} - T\Delta S_{Sys}$$

$$= \Delta G$$

Gibbs free energy is the "extra" energy available to do work! (free here is used in the sense of "available", not "no-cost")

Gibbs Free Energy

Calculate ΔG at 25 ∘C for: 1) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$

$$
\begin{aligned}
\Delta H_{rxn} &= \Delta H_f\left(H_2O_{(l)}\right) - \Delta H_f\left(H_{2(g)}\right) - \frac{1}{2}\Delta H_f\left(O_{2(g)}\right) \\
&= \left(-286 - 0 - \frac{1}{2}\cdot 0\right)\mathrm{kJ}\cdot\mathrm{mol}^{-1} \\
&= -286\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}
\end{aligned}
$$

$$
\begin{aligned}
\Delta S_{rxn} &= S^{o}\left(H_2O_{(l)}\right) - S^{o}\left(H_{2(g)}\right) - \frac{1}{2}S^{o}\left(O_{2(g)}\right) \\
&= \left(70 - 131 - \frac{1}{2}\cdot 205\right)\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1} \\
&= -164\ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}
\end{aligned}
$$

Exothermic

Entropy decreases

$$
\begin{aligned}
\Delta G_{rxn} &= \Delta H_{rxn} - T\Delta S_{rxn} = -286\times 10^{3}\,\mathrm{J}\cdot\mathrm{mol}^{-1} - 298\ \mathrm{K}\cdot\left(-164\ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}\right) \\
&= -237\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}
\end{aligned}
$$

This reaction is spontaneous (enthalpy-driven), and you can achieve up to 237 kJ of work per mole of H_2 combusted.

Gibbs Free Energy

Calculate ΔG at 25 ∘C for: $2)\ H_2O_{(l)} \longrightarrow H_2O_{(g)}$

$$\begin{aligned}\Delta H_{rxn} &= \Delta H_f\left(H_2O_{(g)}\right) - \Delta H_f\left(H_2O_{(l)}\right)\\ &= \left(-241.82 + 285.83\right)\mathrm{kJ}\cdot\mathrm{mol}^{-1}\\ &= 44.01\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}\end{aligned}$$

Endothermic

$$\begin{aligned}\Delta S_{rxn} &= S^{\mathrm{o}}\left(H_2O_{(g)}\right) - S^{\mathrm{o}}\left(H_2O_{(l)}\right)\\ &= \left(188.83 - 69.91\right)\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}\\ &= 118.92\ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}\end{aligned}$$

Entropy increases

$$\begin{aligned}\Delta G_{rxn} &= \Delta H_{rxn} - T\Delta S_{rxn} = 44.01\times 10^3\,\mathrm{J}\cdot\mathrm{mol}^{-1} - 298.15\ \mathrm{K}\cdot\left(118.92\ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}\right)\\ &= 8.55\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}\end{aligned}$$

This reaction is **nonspontaneous** (unfavorable); you would need to **invest at least 8.55 kJ of work per mole of water** to get it into the gas phase at 25 ₒC.

Gibbs Free Energy

Calculate ΔG at 25 °C for: $2)\ H_2O_{(l)} \longrightarrow H_2O_{(g)}$

At what temperature would the reaction become spontaneous?

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = 0$$

$$T = \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{44.01\times10^{3}\,\mathrm{J\cdot mol^{-1}}}{118.92\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}} = 370\ \mathrm{K} \approx 97\ ^{\circ}\mathrm{C}$$

This is close to the actual temperature of 100 °C at which water spontaneously goes from the liquid state to the gas state.

The **deviation** is from the **assumption** that **enthalpy** and **entropy** do **not depend on temperature** (in reality, both ΔH and ΔS **decrease** from 25 °C to 100 °C, but the **deviation in ΔS is larger**).

The 3% error is relatively small.
But could be big enough to cause problems in some cases.

19.7 Free Energy and the Equilibrium Constant

There must be a relationship between the Equilibrium constant and ΔG

For any condition:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

ΔG_f°: the standard free energy of formation

R: the universal gas constant 8.314 J/ mol K

Q: As defined before.

If $Q = K$, the reaction is at equilibrium

If $Q < K$, reaction shifts right to form products

If $Q > K$, reaction shifts left to form reactants

19.7 Free Energy and the Equilibrium Constant

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Under **standard conditions**, concentrations are 1 *M*, so

$Q = 1$ and $\ln\ Q = 0$; the last term drops out.

And at equilibrium, $Q = K$, and $\Delta G = 0$.

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad K = e^{-\frac{\Delta G^\circ}{RT}}$$

Free Energy and the Equilibrium Constant

The standard free energies of formation of dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) are:

$$\Delta G_f^\circ(\mathrm{N_2O_4}) = 97.9\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta G_f^\circ(\mathrm{NO_2}) = 51.3\ \mathrm{kJ \cdot mol^{-1}}$$

$$\mathrm{N_2O_4} \rightleftharpoons \mathrm{2NO_2}$$

1. Calculate the value of ΔG for a system consisting of 0.35 atm NO_2 and 0.50 atm N_2O_4 at 298 K.

2. Calculate the value of K for this system. In which direction will the system move - toward the product or toward the reactant?

Free Energy and the Equilibrium Constant

$$\Delta G_f^\circ(\mathrm{N_2O_4}) = 97.9\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta G_f^\circ(\mathrm{NO_2}) = 51.3\ \mathrm{kJ \cdot mol^{-1}}$$

$$\mathrm{N_2O_4} \rightleftharpoons \mathrm{2NO_2}$$

1. Calculate the value of Δ*G* for a system consisting of 0.35 atm NO_2 and 0.50 atm N_2O_4 at 298 K.

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q$$

So we can calculate both ΔG° and Q

- $\Delta G^\circ_{rxn} = 2 \times \Delta G_f^\circ(\mathrm{NO_2}) - \Delta G_f^\circ(\mathrm{N_2O_4})$

  $= 2 \times 51.3\ \mathrm{kJ \cdot mol^{-1}} - 97.9\ \mathrm{kJ \cdot mol^{-1}}$

  $= 4.7\ \mathrm{kJ \cdot mol^{-1}}$

- $Q = \dfrac{P_{\mathrm{NO_2}}{}^2}{P_{\mathrm{N_2O_4}}} = \dfrac{0.35^2}{0.5} = 0.245$ (remember: no units here!)

Free Energy and the Equilibrium Constant

- $$\begin{aligned}\Delta G^{o}_{rxn} &= 2\times\Delta G^{o}_{f}\left(NO_2\right)-\Delta G^{o}_{f}\left(N_2O_4\right)\\ &= 2\times 51.3\ \text{kJ}\cdot\text{mol}^{-1}-97.9\ \text{kJ}\cdot\text{mol}^{-1}\\ &= 4.7\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

$$\Delta G^{o}_{f}(N_2O_4)=97.9\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta G^{o}_{f}(NO_2)=51.3\ \text{kJ}\cdot\text{mol}^{-1}$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

- $$Q=\frac{{P_{NO_2}}^{2}}{P_{N_2O_4}}=\frac{0.35^2}{0.5}=0.245$$

1. Calculate the value of Δ*G* for a system consisting of 0.35 atm NO2 and 0.50 atm N2O4 at 298 K.

$$\begin{aligned}\Delta G_{rxn} &= \Delta G^{o}_{rxn}+RT\ln Q\\ &= 4.7\times 10^{3}\ \text{J}\cdot\text{mol}^{-1}\\ &\quad +8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\times 298\ \text{K}\times\ln\left(0.245\right)\\ &= 1.2\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

ΔG **is not zero**, so this reaction is **NOT at equilibrium**.
ΔG is **plus**, so the reaction will move in the **reverse reaction** to form more reactants.

Free Energy and the Equilibrium Constant

$$\Delta G_f^{\circ}(\mathrm{N_2O_4}) = 97.9\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta G_f^{\circ}(\mathrm{NO_2}) = 51.3\ \mathrm{kJ \cdot mol^{-1}}$$

$$\mathrm{N_2O_4} \rightleftharpoons \mathrm{2NO_2}$$

2. Calculate the value of *K* for this system.

$$K = e^{\frac{-\Delta G^{\circ}_{rxn}}{RT}} = e^{\frac{-4.7\times10^{3}\ \mathrm{J{\cdot}mol^{-1}}}{8.314\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}\times 298\ \mathrm{K}}} = 0.150$$

an equilibrium where the **reactants are more favored** than the products
(*K* < 1)
Δ*G*o positive

Free Energy and the Equilibrium Constant

$$\Delta G_f^{\mathrm{o}}(\mathrm{N_2O_4}) = 97.9\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta G_f^{\mathrm{o}}(\mathrm{NO_2}) = 51.3\ \mathrm{kJ \cdot mol^{-1}}$$

$$\mathrm{N_2O_4} \rightleftharpoons \mathrm{2NO_2}$$

3. In which direction will the system move toward the product or toward the reactant?

need to compare *Q* and *K* to decide:

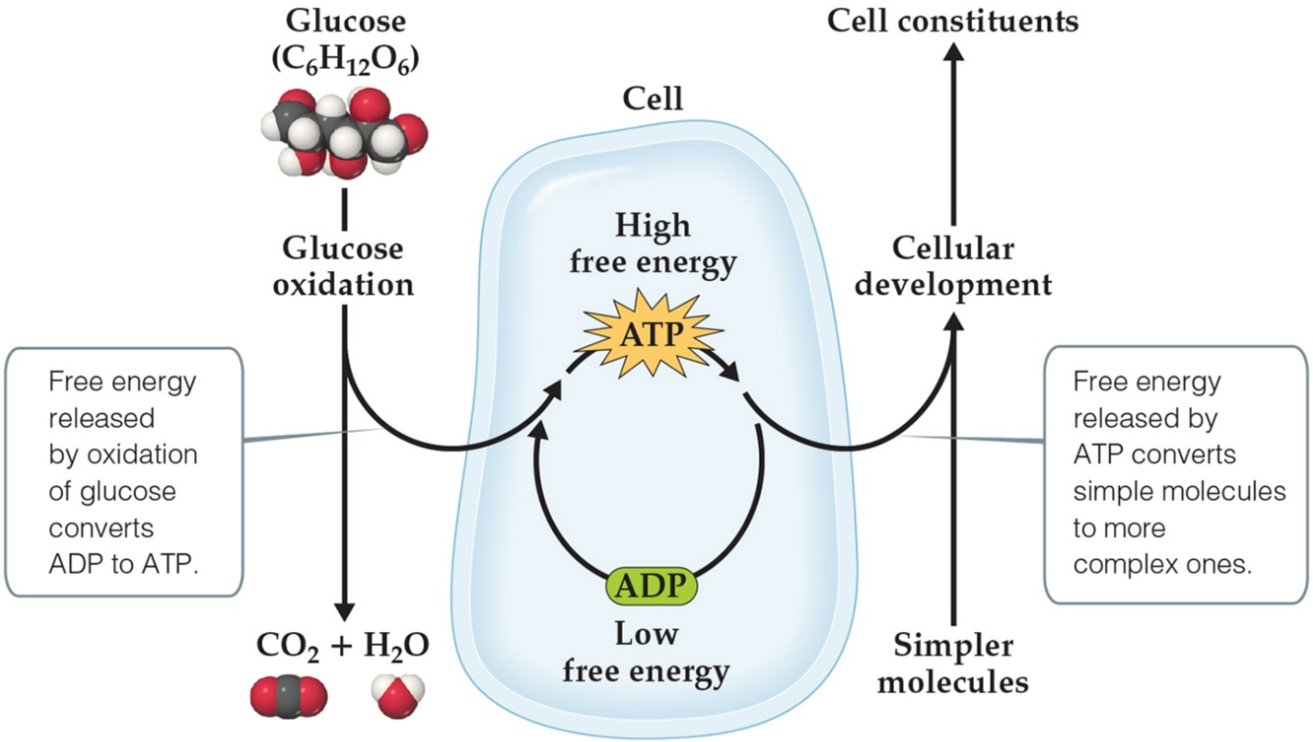
$$K = 0.150 \quad \text{and} \quad Q = 0.245$$

$$\text{so: } Q > K$$

Since ***Q* is bigger**, there is **too much product** and not enough reactant: the reaction will proceed toward the **reactant** (REVERSE DIRECTION).

Driving Nonspontaneous Reactions

- Many desirable reactions are nonspontaneous as written.
- Nature couples reactions, i.e., cell metabolism.

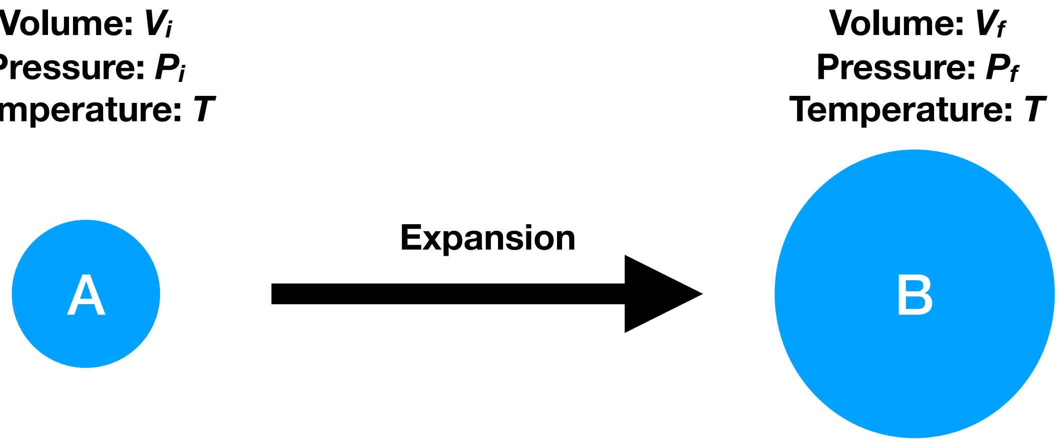


Free energy released by oxidation of glucose converts ADP to ATP.

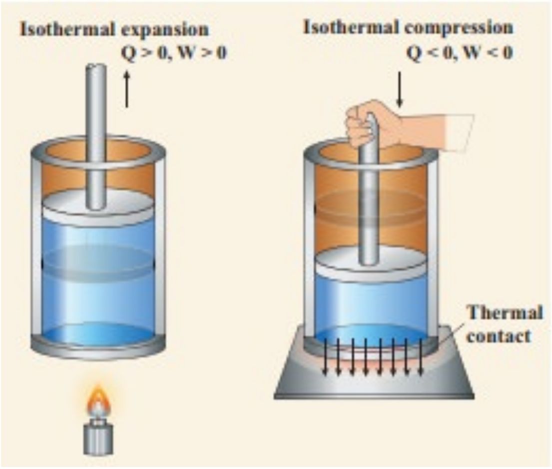
Free energy released by ATP converts simple molecules to more complex ones.

A Simple Problem using the 1st Law of Thermodynamics

“Isothermal expansion of ideal gas”
EXPANSION OF AN IDEAL GAS, NO CHANGE IN TEMPERATURE



How to achieve the isothermal condition?
Efficiently dissipate the heat from the system.



Since the two states of the gas (initial, “A”, and final, “B”) have the **same temperature**, both states A and B MUST have the **same Internal Energy, *E*.**

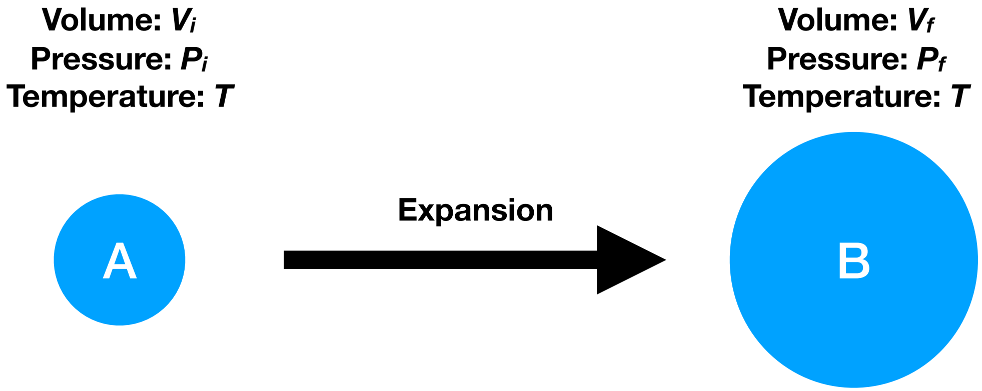
Why?
For ideal gases

$$< v^2 >^{1/2} = v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\Delta E=\Delta K.E.=\Delta(1/2mv_2)$$

A Simple Problem to Learn how to Use the 1st Law of Thermodynamics

“Isothermal expansion of ideal gas”



Volume: V_i
Pressure: P_i
Temperature: T

Volume: V_f
Pressure: P_f
Temperature: T

If the temperature is the same for A and B (”isothermal”), **there is no change in the internal energy:**

$$\Delta E = 0$$

$$\Downarrow$$

But the first law tells us that:

$$\Delta E = q + w$$

Which means that for this process:

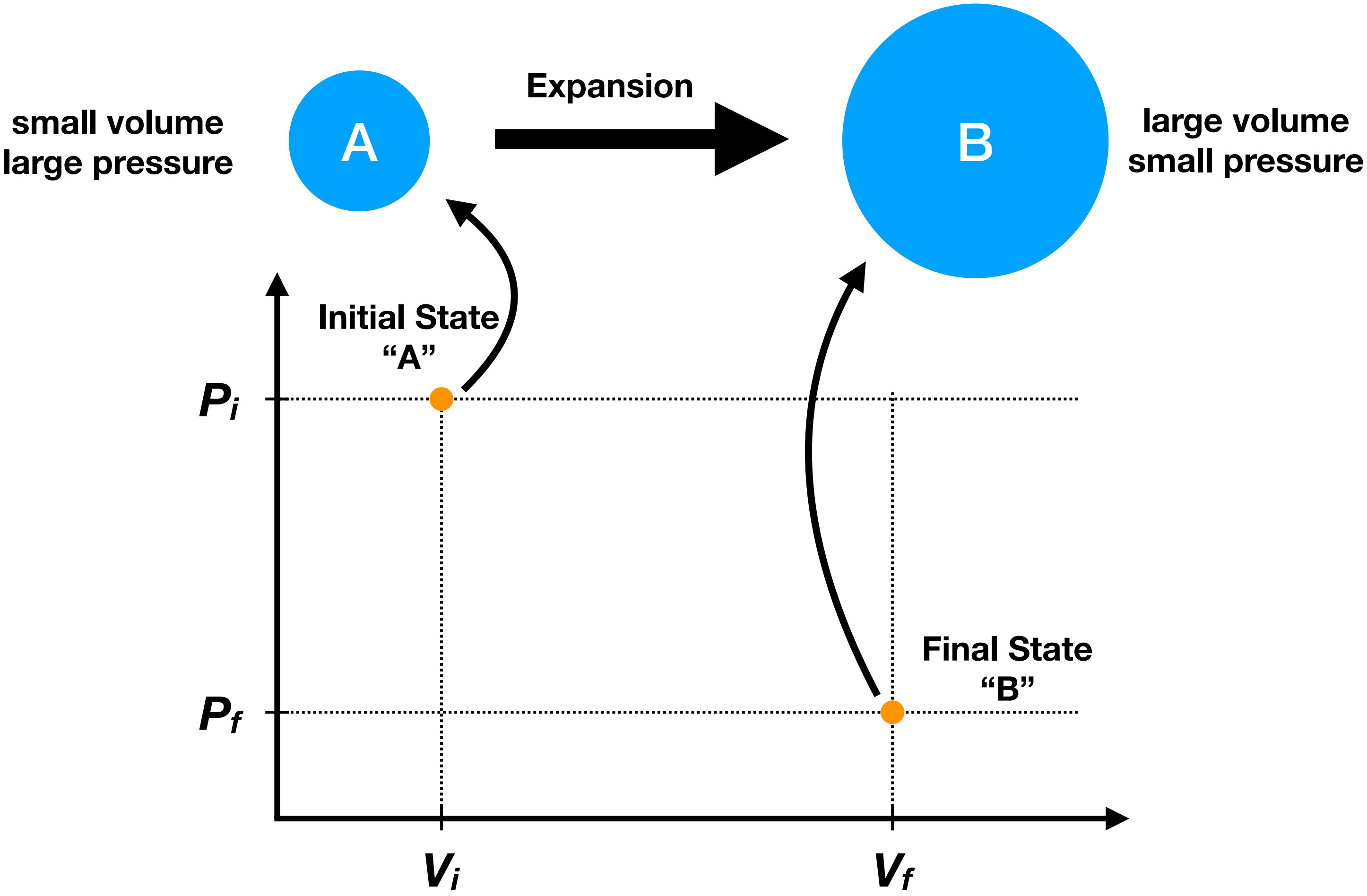
$$w = -q$$

What does this mean? In isothermal expansion, any work done must produce an equal amount of heat. The heat lost in the system is converted to the equal amount of work done on the surrounding.

Using a P-V Graph

“Isothermal expansion of ideal gas”

“Isothermal expansion involves the change in pressure and volume”



small volume
large pressure

Expansion

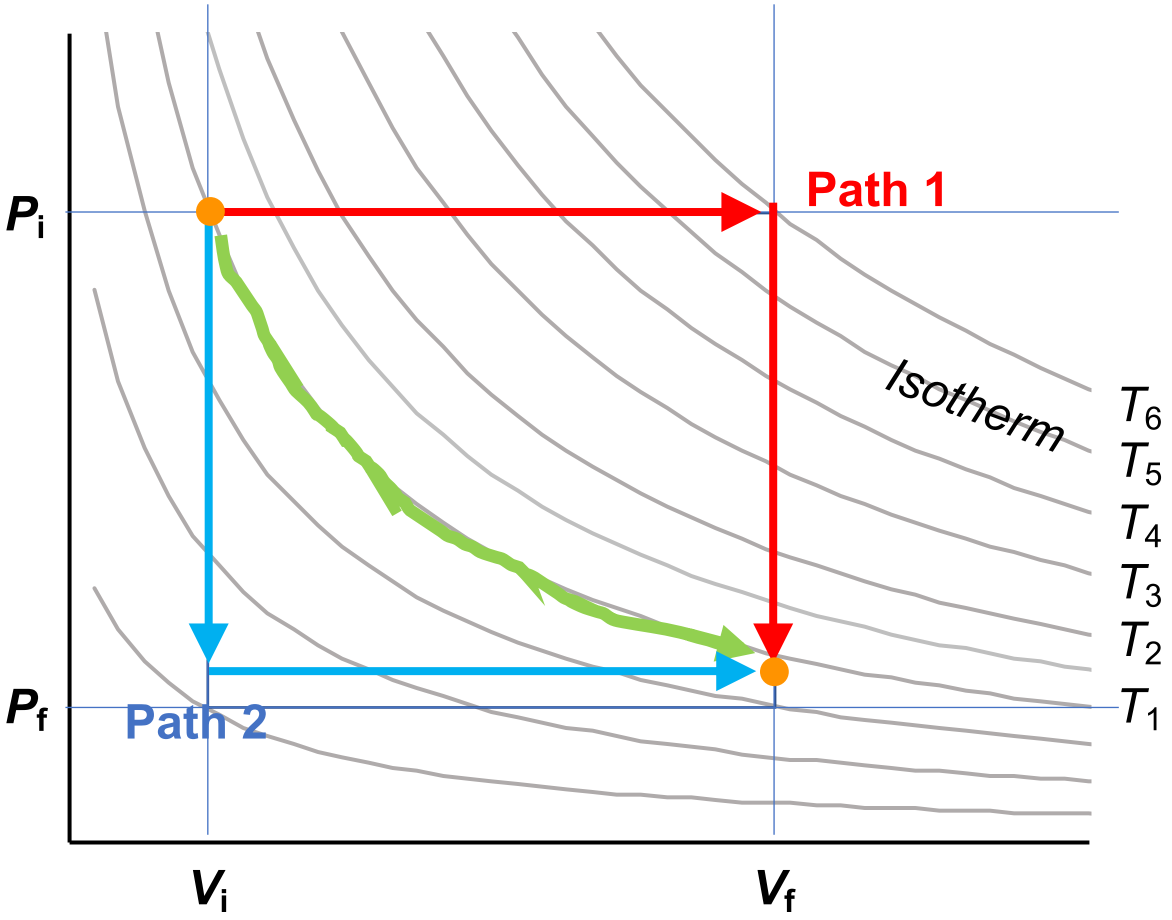
large volume
small pressure

Initial State
“A”

Final State
“B”

Closer look at what's going on in the isothermal expansion

To move from the initial state to the final state via Path 1 or Path 2, the system should pass through different isotherms (that is, temperature should increase or decrease). However, an isothermal process moves along the two states on the same the isotherm.



Each isotherm conforms to the ideal gas equation

$P = nRT/V$

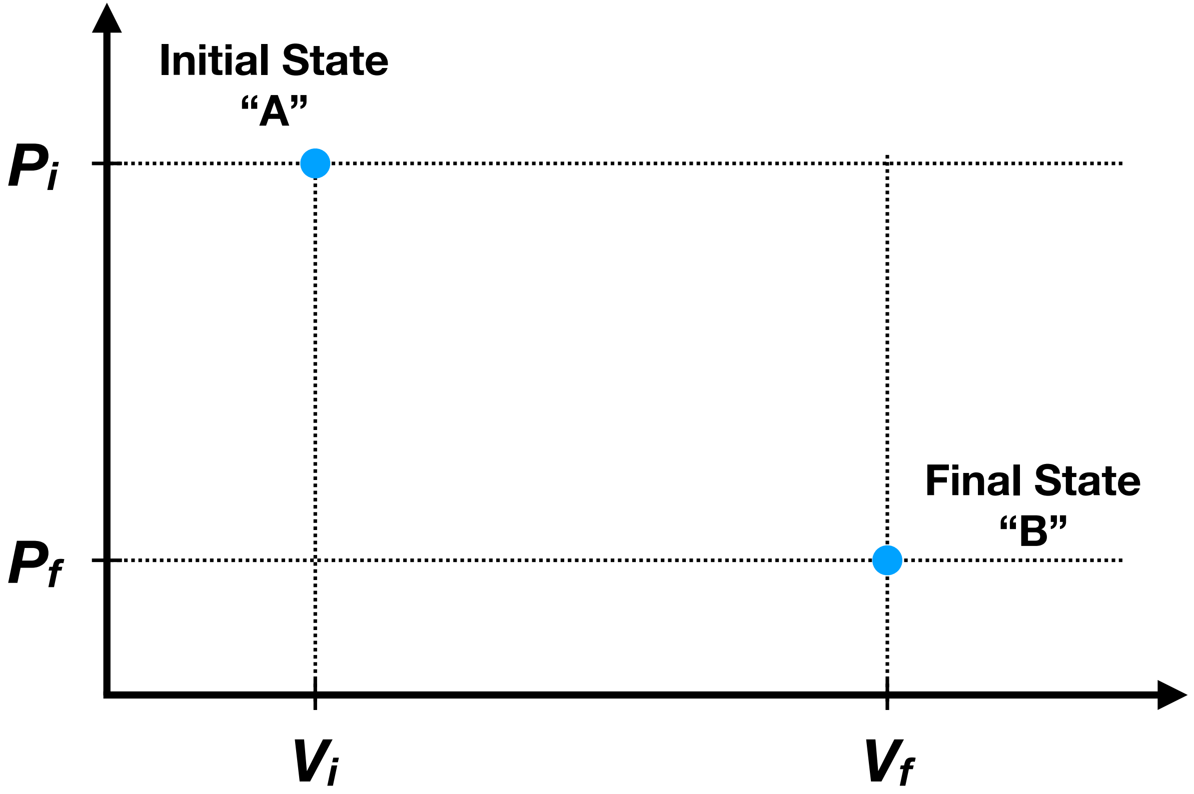
(at a given T)

T increases

Using a P-V Graph

“Isothermal expansion of ideal gas”

There are many ways to connect these two states; each will require a different amount of heat and work, but since the difference in internal energy between state A and B is zero, **the sum of q + w will ALWAYS be zero!**

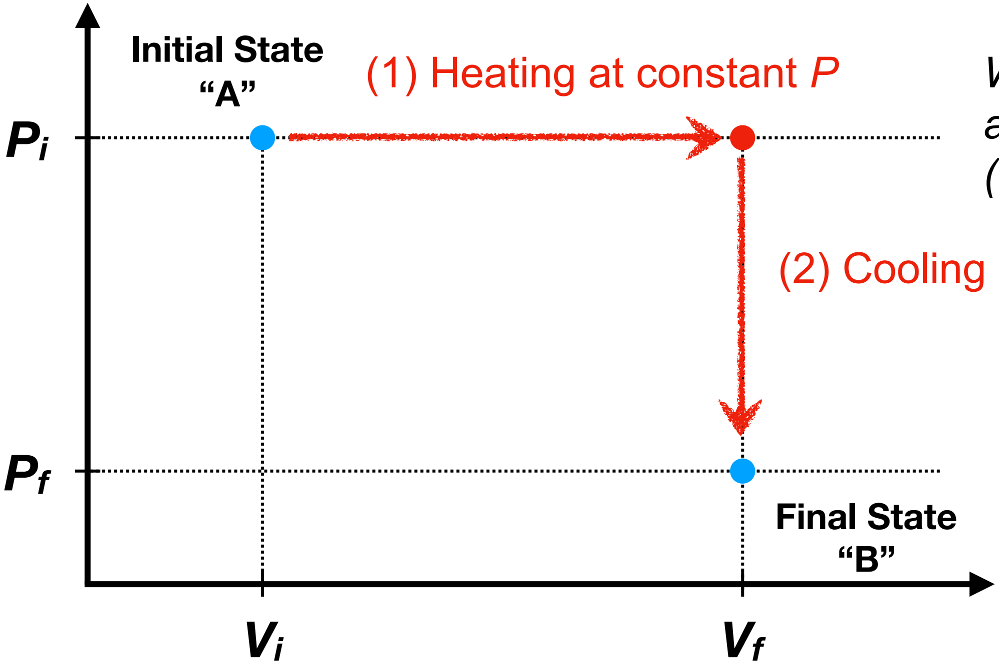


Using a P-V Graph

Here is a FIRST way to connect A to B:

1) Under constant pressure P_i, heat the gas until the volume expands from V_i to V_f;

2) Keeping the volume constant at V_f, cool down the gas back to the original temperature, where the pressure will become P_f.



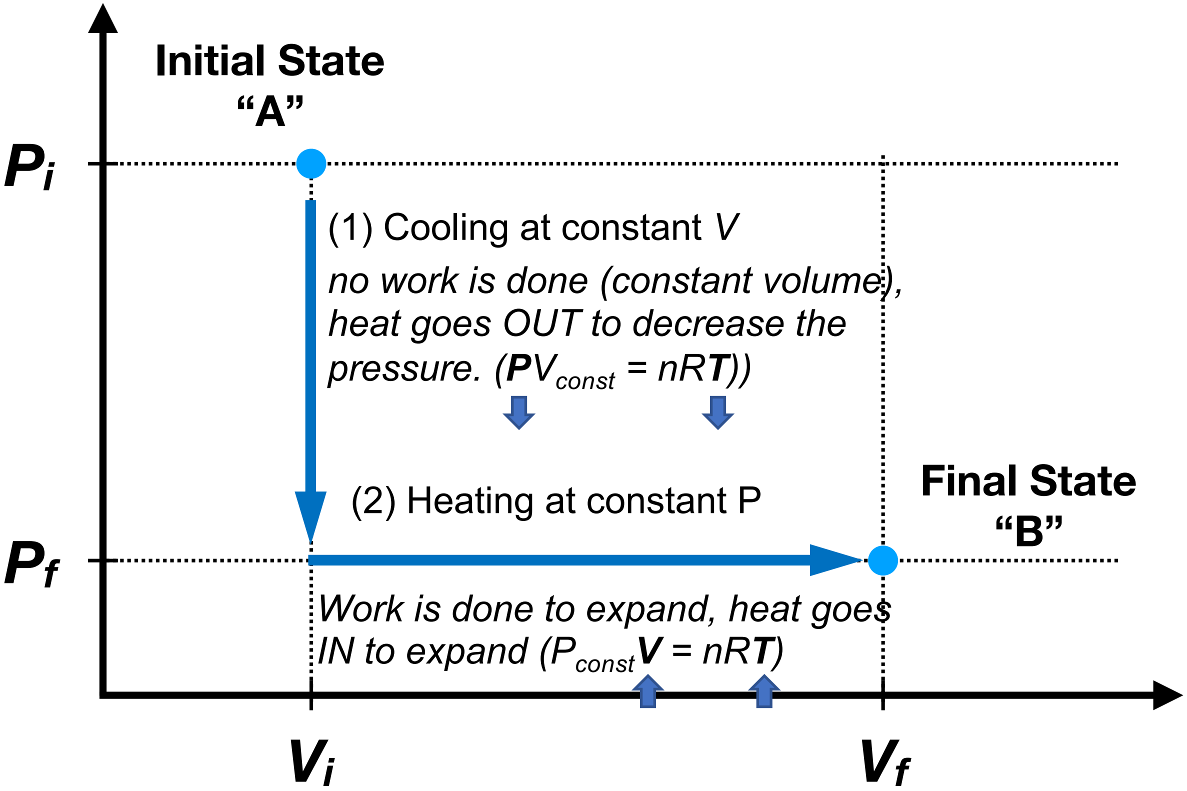
Work is done to expand (V increases) and heat goes IN to expand $(P_{const}\underset{\Uparrow}{\mathbf{V}} = nR\underset{\Uparrow}{\mathbf{T}})$.

No work is done (constant volume), heat goes OUT to decrease the pressure $(\underset{\Downarrow}{\mathbf{P}}V_{const} = nR\underset{\Downarrow}{\mathbf{T}})$.

Using a P-V Graph

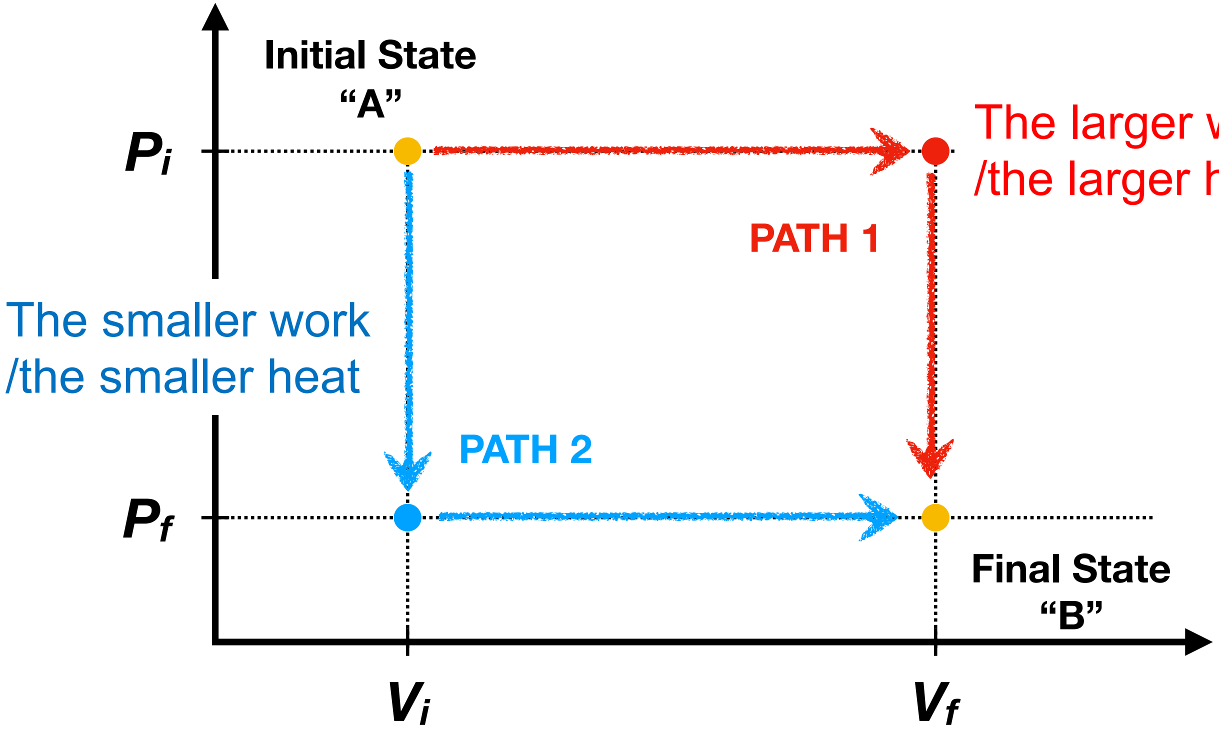
And a SECOND way to connect A to B:

1) Keeping the volume constant at Vi, cool down the gas back until the pressure becomes Pf.
2) Keeping the pressure constant at P_f, heat the gas to the original temperature, where the volume becomes V_f.



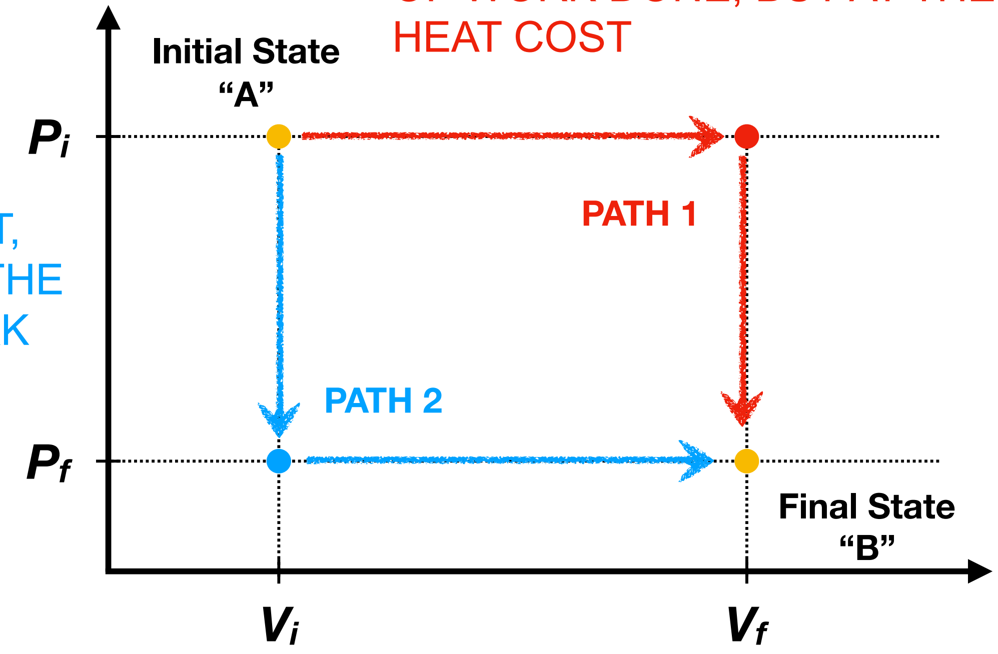
Comparing the Two Paths

- For both, work is done BY the system on the surroundings ($w_{tot} < 0$)
- For both, $w_{tot} = -q_{tot}$, meaning that $q_{tot} > 0$ (more heat goes IN than goes OUT)
- The work in path 2 is SMALLER than in path 1 because the expansion is against a smaller external pressure, that is, $P_f < P_i$ (remind that $w = -P\Delta V$,)
- This means that the net heat that flows IN the system is SMALLER for path 2 than for Path 1. ($\Delta E = q - P\Delta V = 0$. That is, $q = P\Delta V$)



Comparing the Two Paths

- The HISTORY of how we go from State A to State B does not affect the net change in the total energy (ΔE)
- **BUT:** path we take **defines** how much work and heat is released/absorbed.
- The LARGEST amount of WORK done by the system (path 1) COSTS the largest amount of HEAT from the surroundings



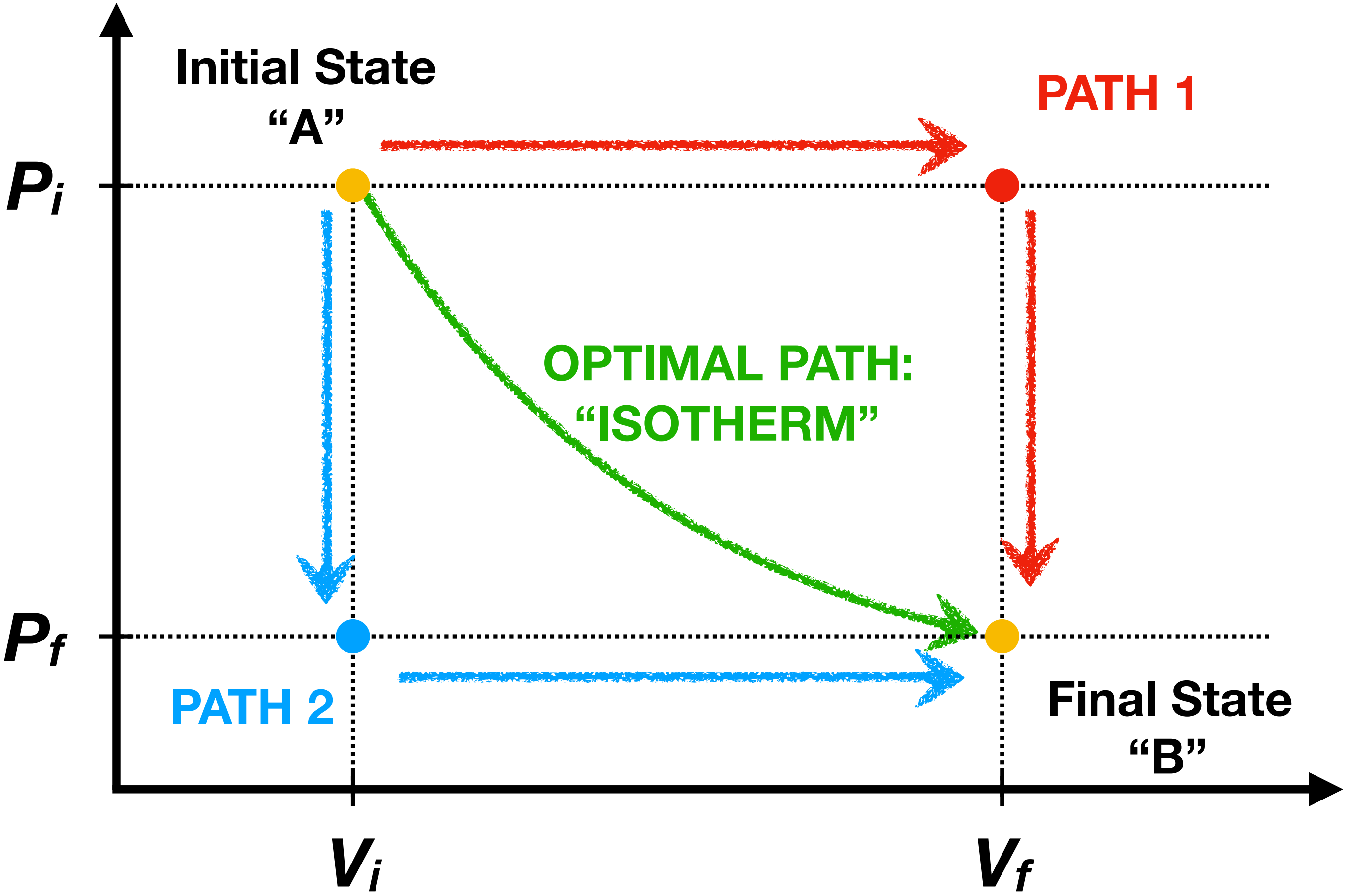
LARGEST AMOUNT OF WORK DONE, BUT AT THE LARGEST HEAT COST

SMALLEST COST IN HEAT, BUT ALSO PRODUCES THE LEAST AMOUNT OF WORK

The "OPTIMAL" Path?

QUESTION: WHAT PATH PRODUCES MAXIMUM WORK FOR MINIMUM HEAT?

ANSWER: THE PATH WHERE THE TEMPERATURE NEVER CHANGES
-THE "**ISOTHERM**" CURVE.



Reversible Processes

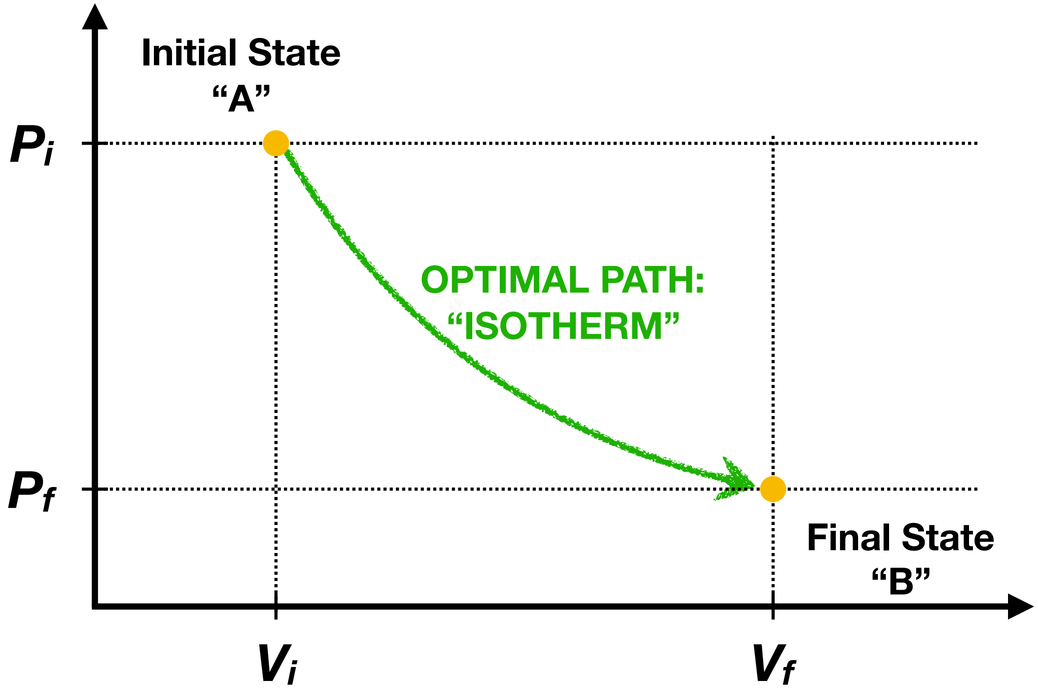
An **ISOTHERMAL EXPANSION**.

-Where the increase in V is perfectly matched by an equivalent decrease in P

PV = nRT. If T constant, P and V must change in perfect concert. Requires infinitesimally small steps.

Under this condition,

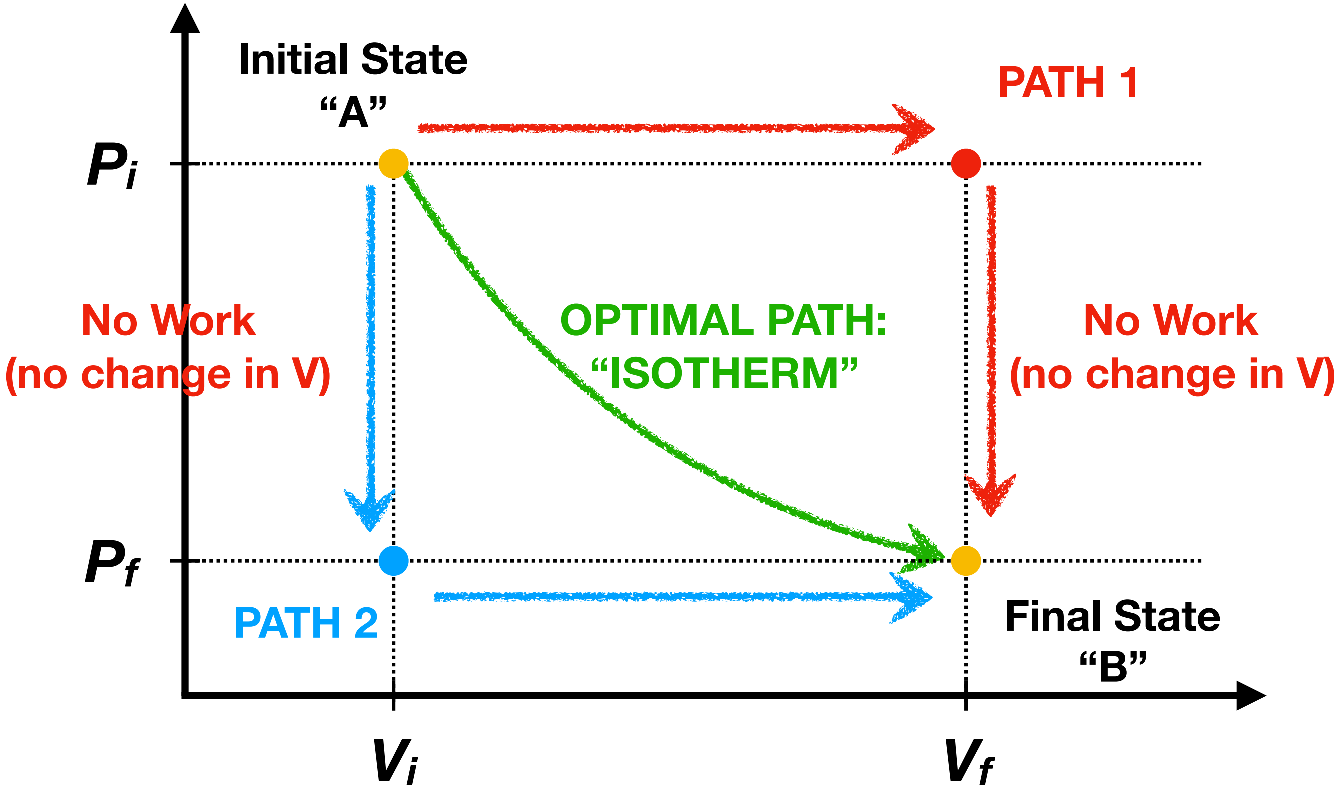
the system will stay in equilibrium with the surroundings all the time.



Reversible Processes

REVERSIBLE PROCESS:
-Correspond to the maximum amount of work you can get out of a system - Because any heat transaction is fully converted into work

Note: In both path 1 and 2 above, some steps involve heat transfer WITHOUT WORK being done: these are examples of irreversible processes.



Reversible Processes

In thermodynamics, **a process where the system remains at equilibrium with the surroundings at every point in time**, like the isothermal expansion described above, is called a **REVERSIBLE PROCESS**.

Reversible processes:

Impossible to realize **perfectly** in real life: -Infinitely small changes take INFINITE TIME!

BUT: if you do the process SLOW enough to let the system adapt to the changes and exchange heat with the surroundings when it needs to, then reversible processes can be approximately obtained.

Two Distinct Types of Reversible Processes

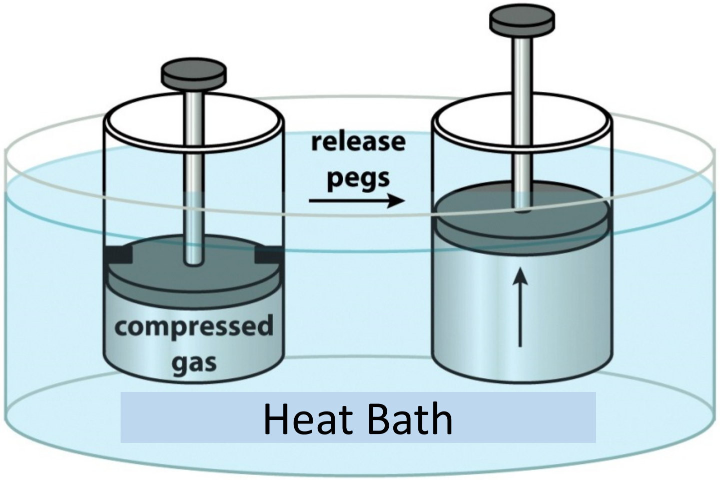
Let's compare the two types of reversible processes
using the compression and expansion of an ideal gas:

$$\Delta E = q + w$$

ISOTHERMAL PROCESS

$$q = -w$$

No temperature change



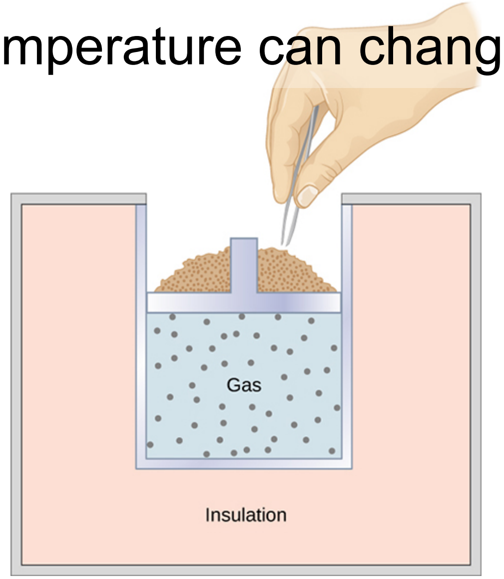
Gas expands or released upon removal of pegs. The temperature of the cylinder is maintained in water bath.

MacMillian, Molecules of Life Kuriyan et al.

ADIABATIC PROCESS

$$\Delta E = \cancel{q} + w = w$$

Temperature can change.



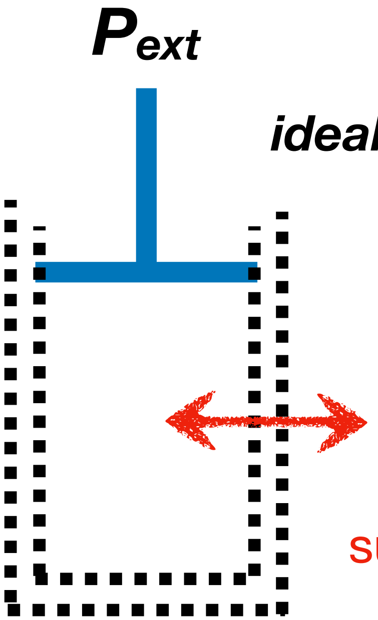
When sand is removed from or added to the piston, the gas expands or compresses adiabatically in the insulated vessel.

https://pressbooks.online.ucf.edu/

Reversible Processes

ISOTHERMAL PROCESS

$$q = -w$$



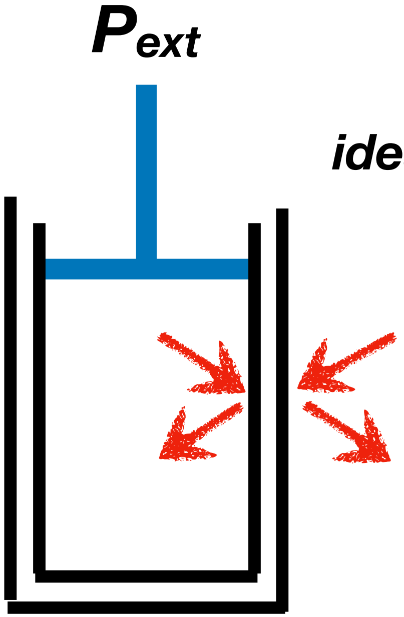
ideal "diathermal" walls

perfect heat transfer to/from surroundings

V*, *P change when ***P**ext* changes, but <u>*T* remains constant.</u>

ADIABATIC PROCESS

$$\Delta E = \cancel{q} + w = w$$



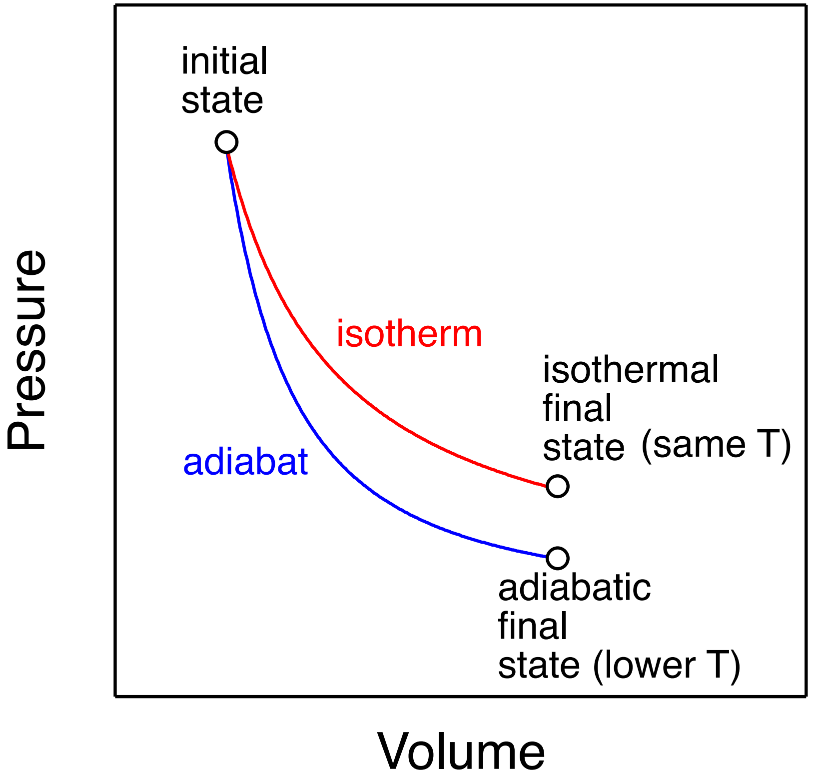
ideal "insulating" walls

no heat transfer to/from surroundings

V*, *P change when ***P**ext* changes, but <u>*T* changes</u> depending on the amount of work done.

Reversible Processes

Let's compare the two types of reversible processes
using the compression and expansion of an ideal gas case:

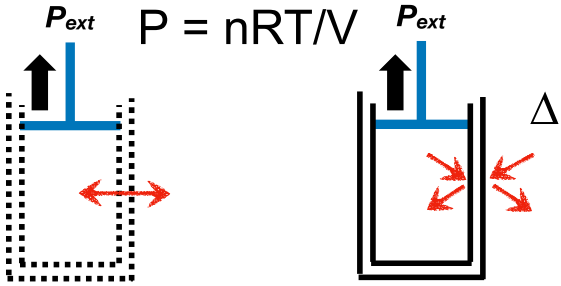


REVERSIBLE GAS EXPANSIONS

The pressure in **Adiabatic EXPANSIONs** always decreases FASTER than in **Isothermal EXPANSIONS**

Why?

The **temperature** should drop at the same time as the volume expands.



$\Delta E = 0$

$P = nRT/V$

$\Delta E = w$

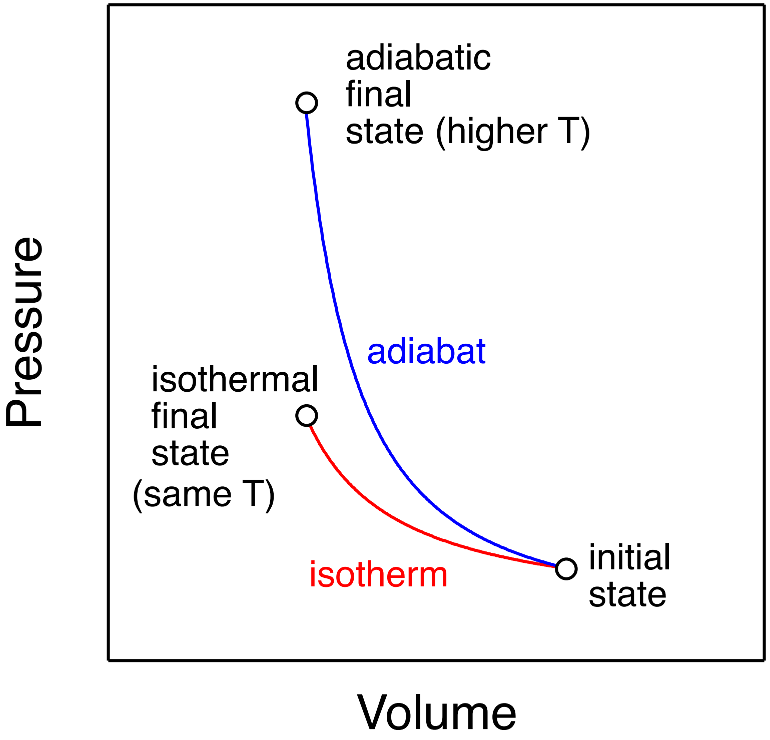
Isothermal
T = same

Adiabatic
T ↓

Reversible Processes

Let's compare the two types of reversible processes using the compression and expansion of an ideal gas case:

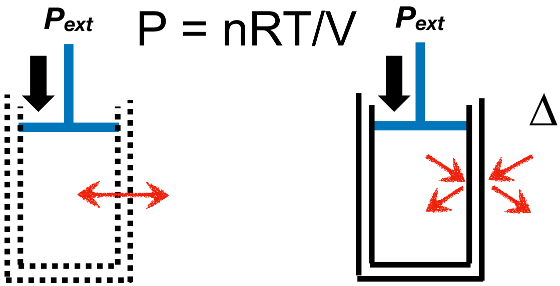
REVERSIBLE GAS COMPRESSIONS



The pressure in **Adiabatic COMPRESSIONS** always increases FASTER than in **Isothermal COMPRESSIONS**

Why?

The **temperature** should increase at the same time as the volume decreases.



$P = nRT/V$

$\Delta E = 0$

$\Delta E = w$

Isothermal
T = same

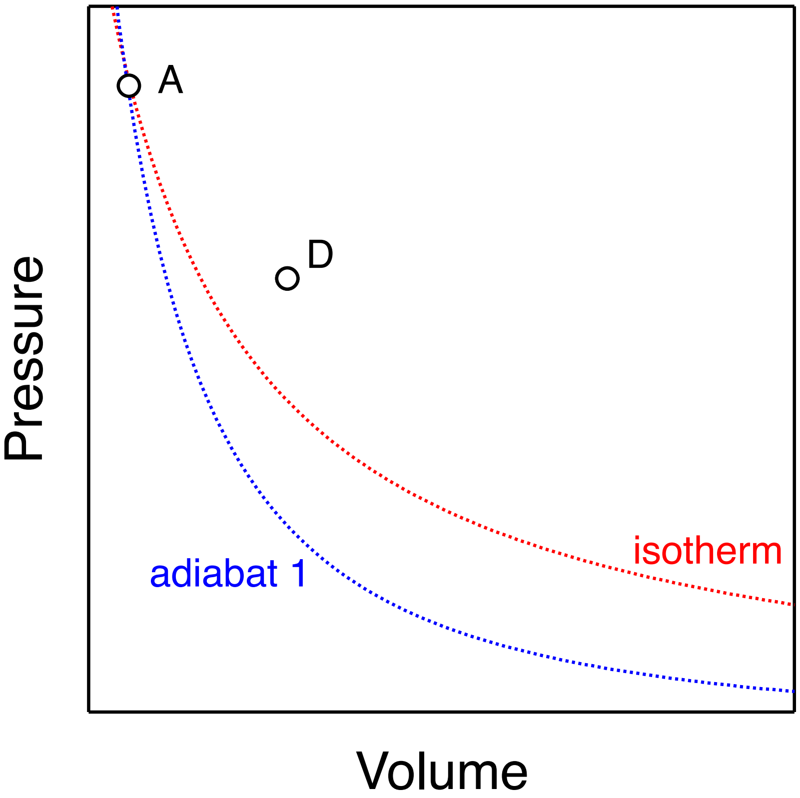
Adiabatic
T = ↑

Reversible Processes

Are there processes which cannot be made reversibly?

NO: you can ALWAYS find a way to connect two states with a reversible path.

Example: Expand an ideal gas from A to D below.



A and D are not connected by either the isotherm or adiabatic paths:

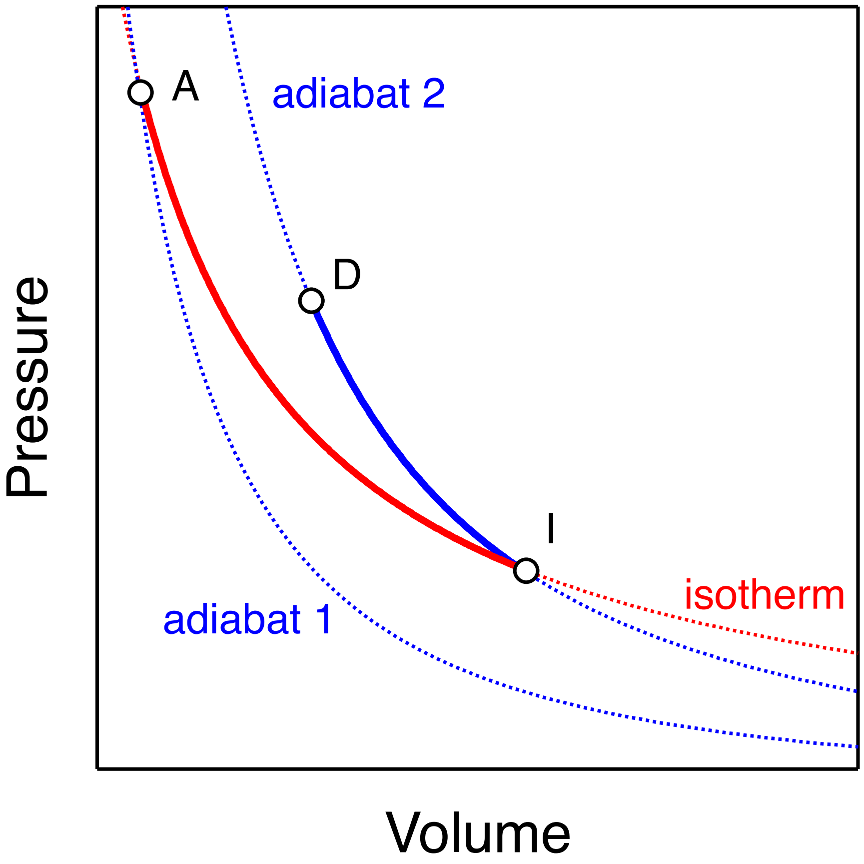
for starters, the temperature of D is HIGHER than the temperature of A?

How can we then go from A to D reversibly, that is:

How can we expand a gas AND heat it, minimizing any heat transfered?

Reversible Processes

Q: How can we then go from A to D reversibly, that is without “wasting” any heat?
A: You go there in two “trips”!



There is more than one way to do this, but here is one:

Step 1) Expand the gas ISOTHERMALLY and reversibly (keep T constant), from State A to intermediate State I.

Step 2) Compress the gas ADIABATICALLY (no heat transfer) and reversibly from State I to State D.

Reversible Processes

The lesson:
We can ALWAYS design a way to go from any state to any other state in a REVERSIBLE manner, without wasting heat.

Note:
Reversible changes need to be done infinitely slowly: if the change is too large and done too fast, then the system does not have enough time to adjust to the change.

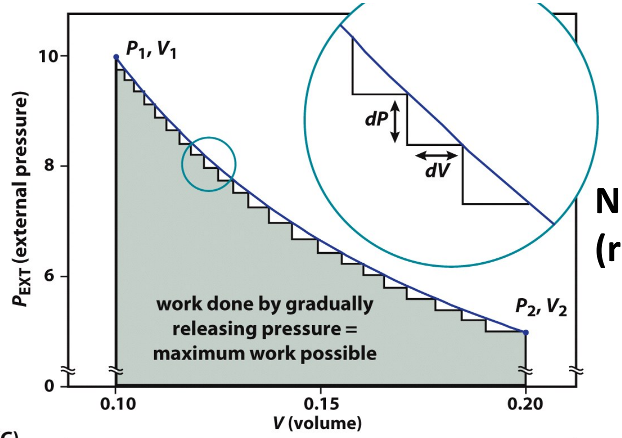
The changes need to be infinitesimally small. That is, theoretically, **reversible changes require an infinite amount of time** to accomplish.

In real life processes;
There are always losses due to friction, electrical resistance, imperfect insulations, etc... which all prevent changes to be perfectly reversible. These non-ideal effects all lead to **heat "waste"**.

Isothermal vs Adiabatic: which reversible pathway does more work?

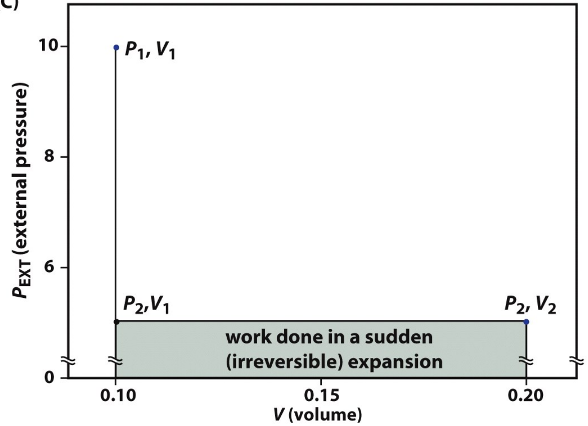
Work (w) = PΔV

w can be obtained by calculating the area under P-V curve.

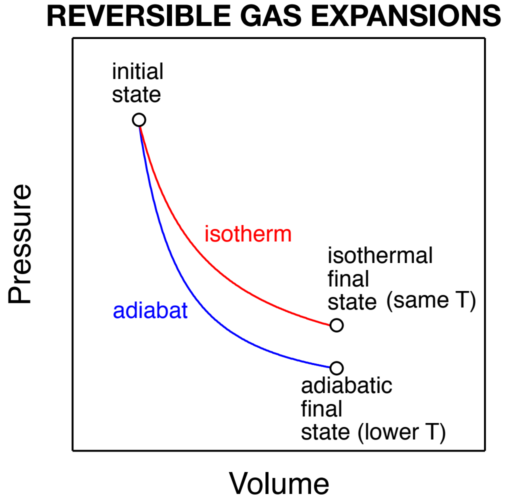


Near-equilibrium (reversible)

(C)



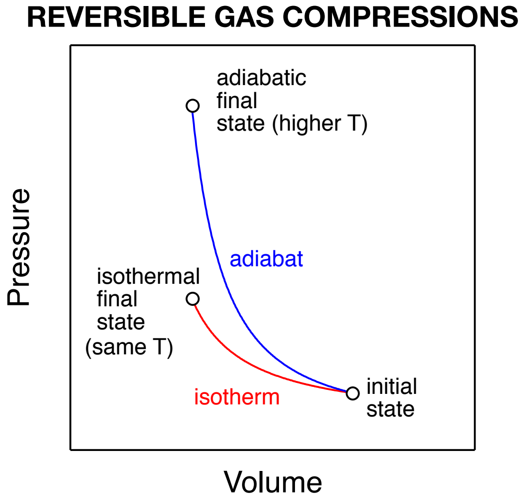
Non-equilibrium (nonreversible)



For the same volume change,

Which gives more work?

Isothermal expansion

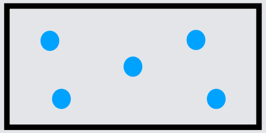


Which gives more work?

Adiabatic compression

The Direction of Change

Any physical or chemical processes have a tendency to going from one to the other SPONTANEOUSLY (without any input).

STATE A	STATE B	DIRECTION OF CHANGE
liquid water at 20 ^{o}C	solid water (ice) at 20 ^{o}C	**B → A**
iron + oxygen	rust	**A → B**
liquid water + solid salt	salted water	**A → B**
 gas molecules everywhere	 gas molecules all in corner of box	**B → A**

The Direction of Change

Spontaneous Process:

A process which occurs on its own, without external influence.

Note: To be spontaneous, the change does NOT need to be fast, or even measurable.

What determines this direction?
Why one way only and not the other??

Maybe its Energy? Go from higher to lower E?

Not always: for example, solid water in 20 ^{o}C to liquid water in 20 ^{o}C

If Energy does not decide direction, what does??

A spontaneous process always increases the "dispersal" of energy...

ENTROPY

Entropy

2nd LAW of THERMODYNAMICS

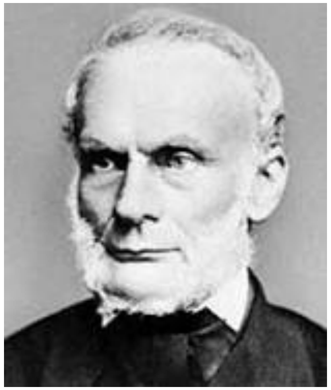
Spontaneous processes are those where the energy "dispersal" of the universe increases, *or* *"the ENTROPY of the universe always increases"*

How do we measure ENTROPY?

"Clausius Equation"

$$\boxed{\Delta S = \frac{q_{rev}}{T}}$$

Note: Heat corresponds to ***disordered motion***, whereas ***work*** induces ***uniform motion*** towards the surroundings. Thus, this equation tells us that "**heat**" measures "**disorder**".



Rudolf Clausius
1822-1888

The ENTROPY CHANGE is the energy transferred as HEAT during a REVERSIBLE PROCESS, DIVIDED by the TEMPERATURE during that process.

Dividing by T means that the entropy generated from heat is large when T is small! That is, dividing by T means the scaling of heat dispersal using temperature.

Statistical Definition of Entropy

ENTROPY is a measure of the number of different ways energy can be distributed.

Ludwig Boltzmann
1844-1906

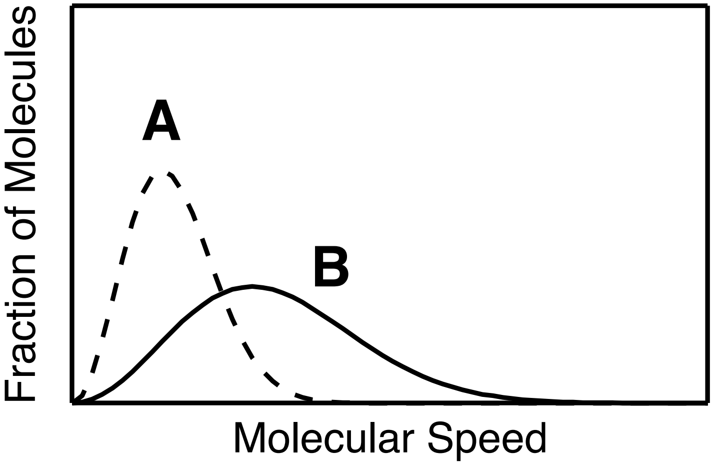
"Boltzmann Equation"

$$\boxed{S = k \ln W}$$

W : # of arrangements (degeneracy), or "microstates"
k : Boltzmann Constant
N_A: Avogadro's number

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$$

What is the unit of entropy? **J·K^{-1}**



These curves are called Boltzmann distributions.

Which state has a large entropy (A or B)?

The broader peak means the larger Entropy

Statistical Definition of Entropy

ENTROPY is a measure of the number of different ways energy can be distributed.

Ludwig Boltzmann
1844-1906

"Boltzmann Equation"

$$\boxed{S = k \ln W}$$

W : # of arrangements (degeneracy), or "microstates"

k : Boltzmann Constant

NA: Avogadro's number

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$$

The **ENTROPY** (not the change!) is proportional to the number of possible arrangements that lead to the same total energy.

The **ENTROPY change:**

$$\Delta S = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For a large number of atoms, the state with maximal multiplicity is the state that is observed at equilibrium.

Microstate

Particular configuration of the atoms or molecules in a system.
“instantaneous snapshot of a system”

State

A global description of the system in terms of its bulk properties.
Not care about what any individual atoms/molecule is doing.

Multiplicity (= “W”)

Number of microstates. A property that determines whether the system is likely to move from one state to another.

The greater the multiplicity associated with a state, the greater the likelihood that we will observe that state.

→ Systems move spontaneously towards states of increasing multiplicity that are consistent with conservation of matter and energy.

The multiplicity of a molecular system and the number of equivalent configurations of the molecules (microstates)

Multiplicity is crucial to understanding the direction of spontaneous change in molecular system.

Multiplicity of a molecular system
The number of different configurations or conformations of the component atoms or molecules that are equivalent.

6 atoms of ideal gas in 7x7 grid

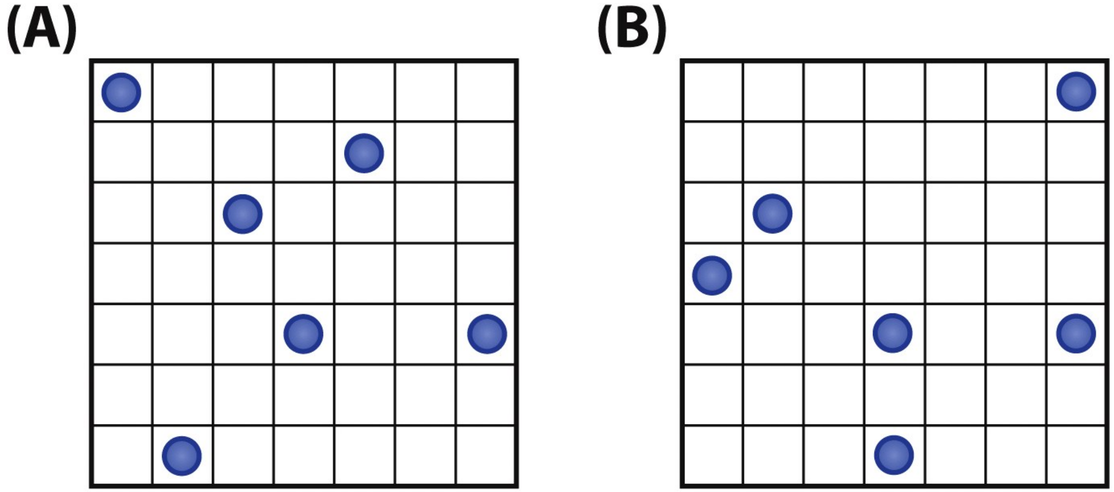


Figure 7.21 The Molecules of Life (© Garland Science 2013)

Multiplicity (W) of the system

$$W(M,N) = \frac{M!}{N!\,(M-N)!}$$

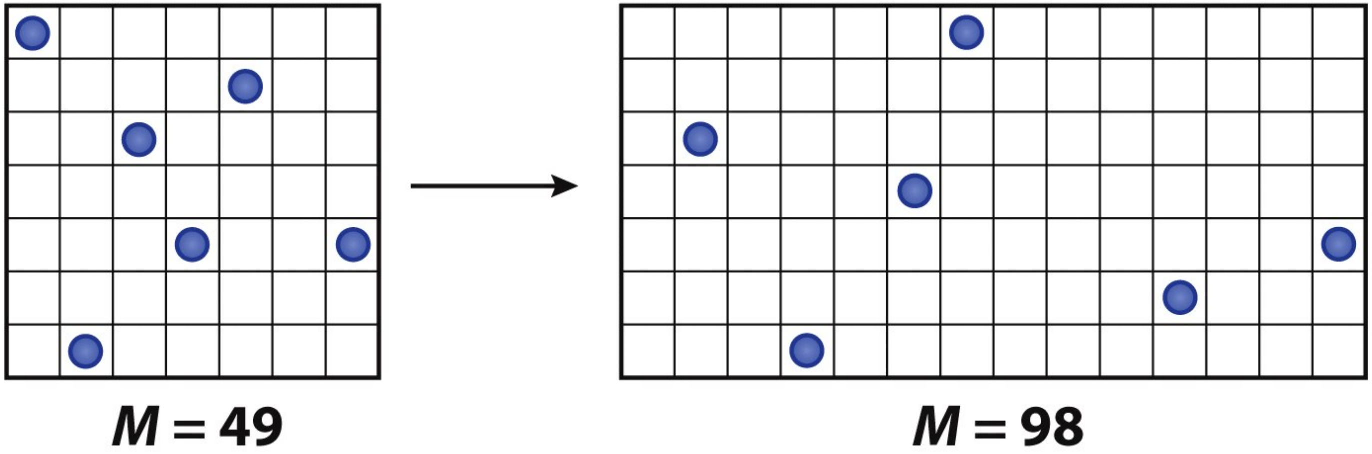
M: number of grids

N: number of atoms

You don't have to worry about this equation.
This is just for your understanding.

Multiplicity and the system volume

$W(49,6) \sim 1.4 \times 10^7$ $\qquad$ $W(98,6) \sim 10^9$



2 times of volume
Keep the grid size

There are ~100 times more possibility to see the atoms spread over the whole grids (which system has the larger entropy ($S = k_B \ln W$)?.

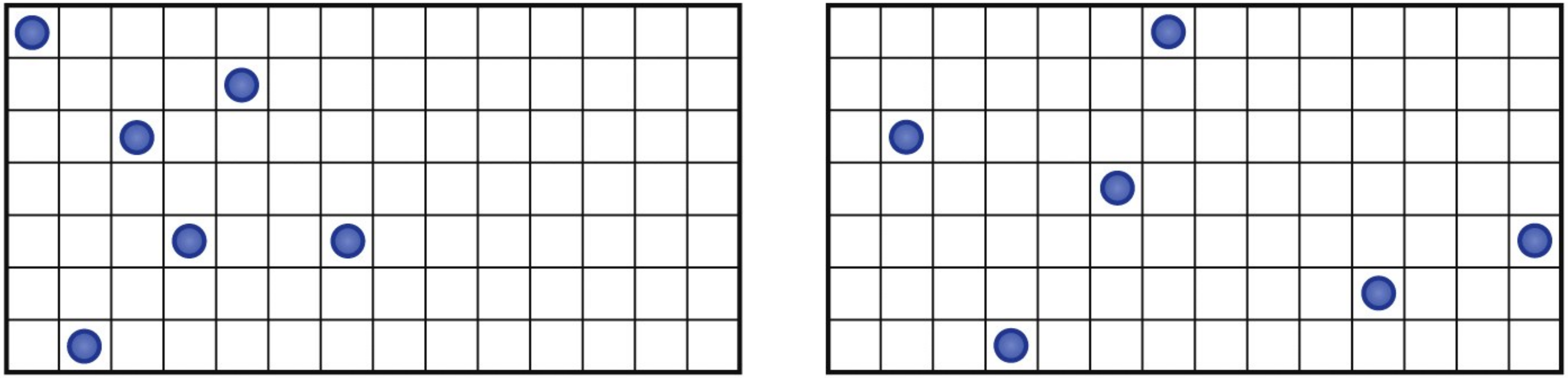
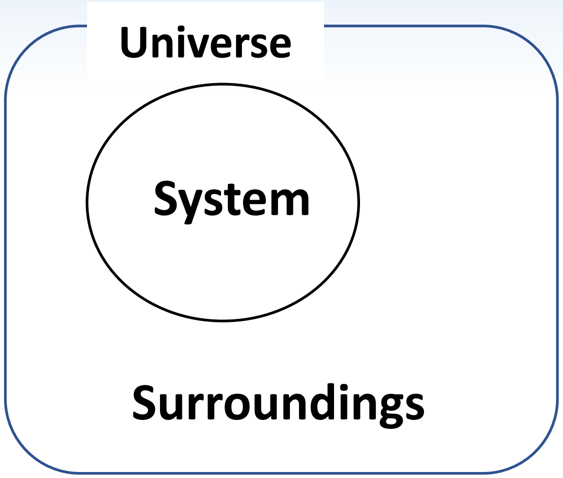


Figure 7.23 The Molecules of Life (© Garland Science 2013)

Laws of Thermodynamics



1st Law: “The energy of the universe is constant”
“You can’t get something for nothing”

$$\Delta E = q + w$$

2nd Law: “The entropy of the universe increases”
“You can’t break even”

$$\Delta S_{univ} = \underbrace{\Delta S_{sys} + \Delta S_{sur}}_{\textbf{that sum must increase}} \geq 0$$

It is the TOTAL entropy change of the universe that dictates the direction of change **NOT the entropy change of the system!**

Even if the entropy of the system decreases, if that of the surrounding increases MORE, the entropy of the universe still increases, so that process can occur spontaneously.

Spontaneous Changes

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} \geq 0$$

We must keep track of entropy changes of both system AND surrounding to predict the change. But how to keep track of both?

Clue: The entropy change of the surroundings is related to the total heat transfer between the system and the surroundings:

Heat transfer (*q*) to the surrounding = Increase of the entropy of the surrounding:

the heat into the surroundings

the heat leaving the system (at constant P)

Clausius equation: $$\Delta S_{sur} = \frac{q_{sur}}{T} = \frac{-\Delta H_{sys}}{T}$$

Note: The negative sign here indicates the heat going INTO the surrounding, that is, the heat LEAVING the system (or vice versa).

Spontaneous Changes

THUS:

$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} \geq 0$$

$$\Delta S_{sur} = \frac{q_{sur}}{T} = \frac{-\Delta H_{sys}}{T}$$

OR:

multiply by -1
on both sides

$$\frac{\Delta H_{sys}}{T} - \Delta S_{sys} \leq 0$$

THIS IS THE CRITERION FOR A SPONTANEOUS REACTION!

OR:
multiply by T
on both sides

$$\boxed{\Delta H_{sys} - T \cdot \Delta S_{sys} \leq 0}$$

at constant P
and constant T

This is equivalent to the 2nd law (only at constant P and T),
but is described only in terms of the system!!

Spontaneous Changes

$$\boxed{\Delta H_{sys} - T \cdot \Delta S_{sys} \leq 0}$$

at constant P
and constant T

Spontaneity of a reaction is determined by three aspects:

1) the sign and size of ΔH
2) the sign and size of ΔS
3) temperature

GREEN = favorable!
RED = unfavorable!

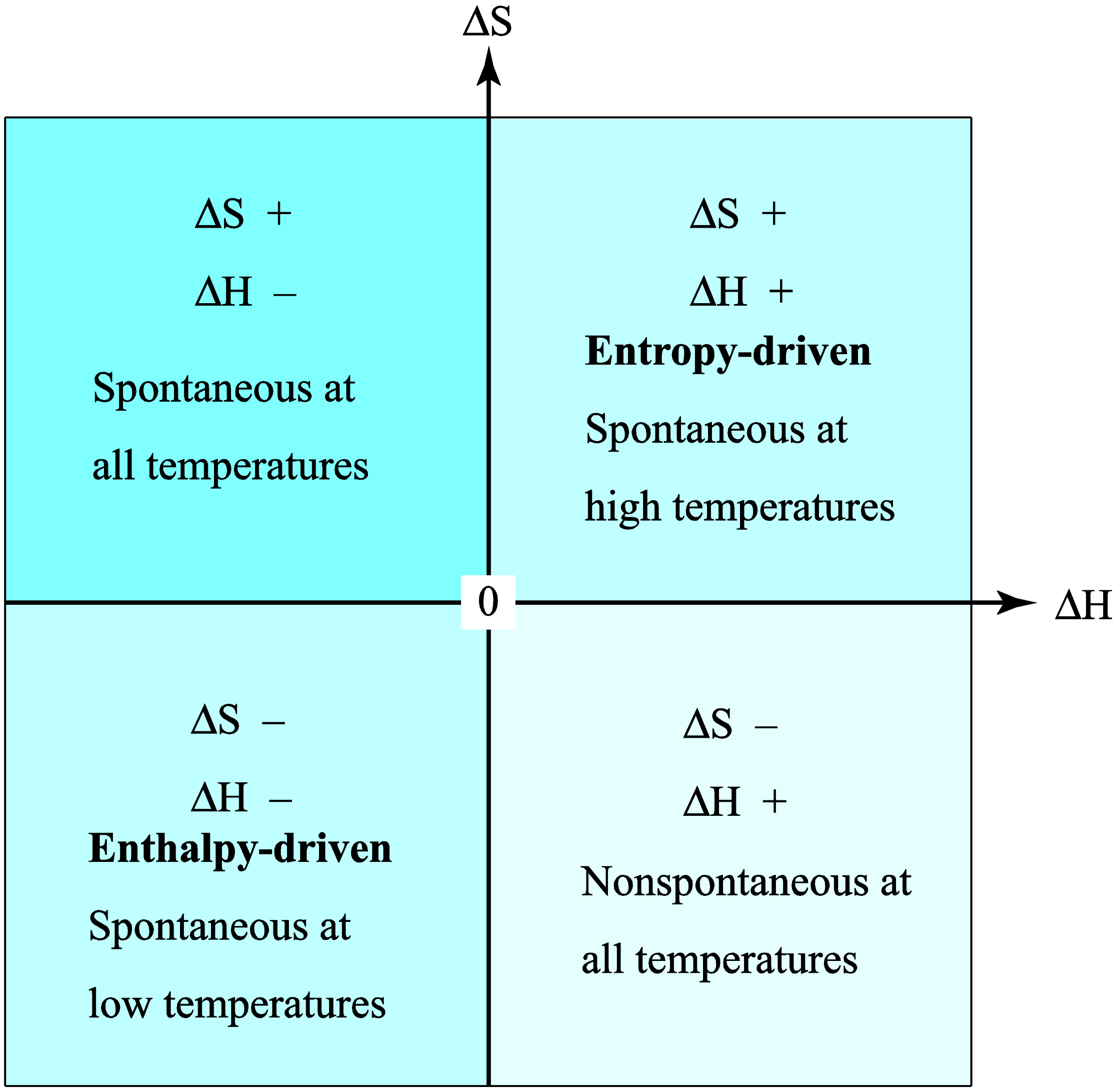
- If both ***ΔH* < 0** and ***ΔS* > 0** : SPONTANEOUS at ALL temperatures!

- If ***ΔH* < 0** but ***ΔS* < 0**: ENTHALPY-DRIVEN process. Favored by LOWER T.

- If ***ΔH* > 0** but ***ΔS* > 0**: ENTROPY-DRIVEN process. Favored by HIGHER T.

- If ***ΔH* > 0** and ***ΔS* < 0**: NOT SPONTANEOUS at ALL temperatures.

Spontaneous Changes



ΔS +

ΔH –

Spontaneous at all temperatures

ΔS +

ΔH +

Entropy-driven

Spontaneous at high temperatures

ΔS –

ΔH –

Enthalpy-driven

Spontaneous at low temperatures

ΔS –

ΔH +

Nonspontaneous at all temperatures

Spontaneous Reactions

Are these processes enthalpy-driven, entropy-driven, or both?

1) Water evaporates at 25 °C;

2) H_2 gas reacts with O_2 gas explosively to form liquid water;

3) An ice pack is activated by mixing a salt (NH_4NO_3) into water.

Spontaneous Reactions

Are these processes enthalpy-driven, entropy-driven, or both?

First, write the chemical reaction. Then, find out the enthalpy and entropy changes (remember! $\Delta X = X_{\text{products}} - X_{\text{reactants}}$)

1) Water evaporates at 25 ^{o}C;

$H_2O_{(l)} \rightarrow H_2O_{(g)}$

ΔH : + (endothermic);
ΔS : + (liquid becoming gas)

ENTROPY-DRIVEN

2) hydrogen gas reacts with oxygen gas explosively to form liquid water;

$H_{2(g)} + 1/2\ O_{2\ (g)} \rightarrow H_2O\ _{(l)}$

ΔH : - (exothermic);
ΔS : - (gas becoming liquid)

ENTHALPY-DRIVEN

3) An ice pack is activated by mixing a salt (ammonium nitrate) into water.

$NH_4NO_{3\ (s)} \rightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$

ΔH : + (endothermic)
ΔS : + (solid salt becoming solubilized)

ENTROPY-DRIVEN

Gibbs Free Energy

Define a new quantity, **ΔG** called the "**GIBBS FREE ENERGY**":

Willard Gibbs, 1839-1903

$$\Delta G = \Delta H - T \cdot \Delta S$$

Like enthalpy and entropy, Gibbs free energy is a state function, does not depend on the way the change is made.

A CRITERION FOR A SPONTANEOUS REACTION:

$\Delta G < 0$: SPONTANEOUS (FAVORABLE)

$\Delta G = 0$: FORWARD and BACKWARD at the same rate

$\Delta G > 0$: NONSPONTANEOUS (UNFAVORABLE)

Temperature Dependence of Δ*G*

How can we determine the temperature at which a process goes from being non-spontaneous (not happening) to being spontaneous (happening)?

By calculating the temperature at which Δ*G* = 0

$$\Delta G_{transition} = 0$$

When the transition (from spontaneous to non-spontaneous, vice versa) happens.

$$\Delta H - T_{transition} \cdot \Delta S = 0$$

$$T_{transition} = \frac{\Delta H}{\Delta S}$$

Important assumption:
Entropy and enthalpy are temperature-independent (an approximation).
Ideally, we would need the values of Δ*H* and Δ*S* measured at the temperature of the transition.

Gibbs Free Energy

	$\Delta H_f^\circ\ \left(\text{kJ}\cdot\text{mol}^{-1}\right)$	$S^\circ\ \left(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\right)$
O_2 (*g*)	**0**	**205.138**
H_2 (*g*)	**0**	**130.684**
H_2O (*l*)	**-285.83**	**69.91**
H_2O (*g*)	**-241.82**	**188.83**

Calculate ΔG at 25 °C for:

$$1)\ \mathrm{H}_{2(g)} + \frac{1}{2}\mathrm{O}_{2(g)} \longrightarrow \mathrm{H_2O}_{(l)} \qquad 2)\ \mathrm{H_2O}_{(l)} \longrightarrow \mathrm{H_2O}_{(g)}$$

If nonspontaneous, estimate the temperature where the reaction becomes spontaneous