Thermodynamics

- Industrial revolution in the late 1700s or early 1800s

- Up till then, heavy work was performed by horses: horsepower

- Fantastic new invention: Heat Engine,

- Thermodynamics: to gain the maximum efficiency from such heat engines

Thermodynamic Definitions

Thermodynamic System

- A thermodynamic system is defined as any part of the Universe under consideration.

- It may be something as similar as a beaker of water, a chemical reaction taking place in a test tube, oil refinery or as complicated as an entire galaxy.
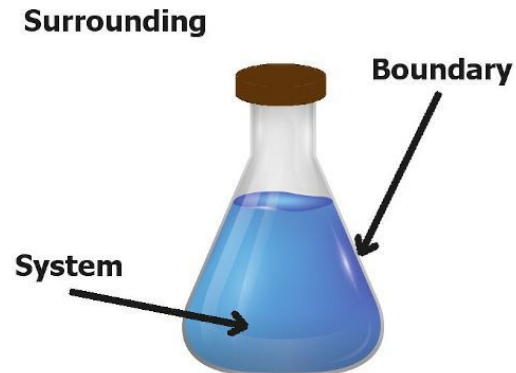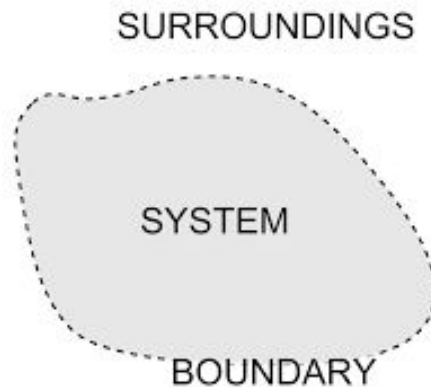
Thermodynamic Definitions

Thermodynamic Surroundings

- Thermodynamics surroundings are defined as everything other than the thermodynamic system.

- In other words, the entire rest of the universe.
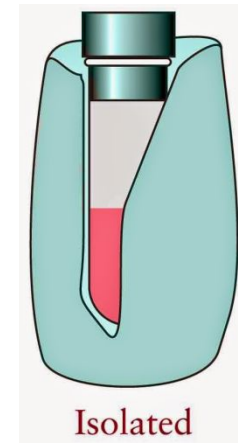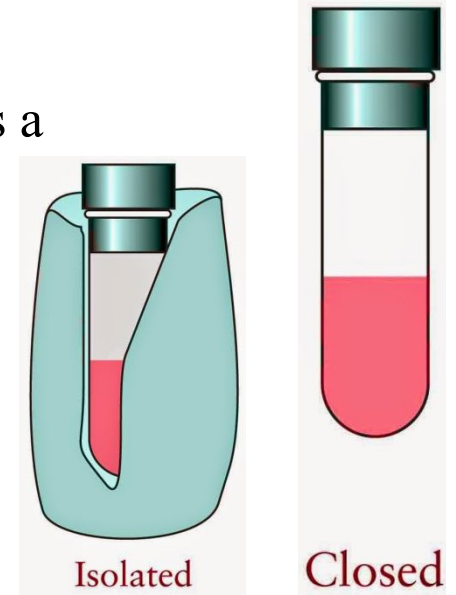
The Universe

- The universe is therefore the system plus the surroundings.

Thermodynamic Definitions

Open, Closed, and Isolated Systems

- **Open System:** An open system may exchange both energy and matter with its surroundings. Changes in composition are therefore possible.

- **Closed System:** A closed system may exchange energy but not matter with its surroundings. Pressure build-up is a distinct possibility.

- **Isolated System:** An isolated system may exchange neither energy nor matter with its surroundings. Pressure build-up is a possibility.

Open

Isolated   Closed

Thermodynamic Definitions

Thermodynamic Surroundings

- Surroundings are assumed to be infinite and remain at constant temperature and pressure.

- The vast size of the universe validates this assumption.

Boundary Conditions

- The boundary may be actual or notional.

- It controls transfer of work, heat, and matter from the system to the surroundings and *vice-versa*.

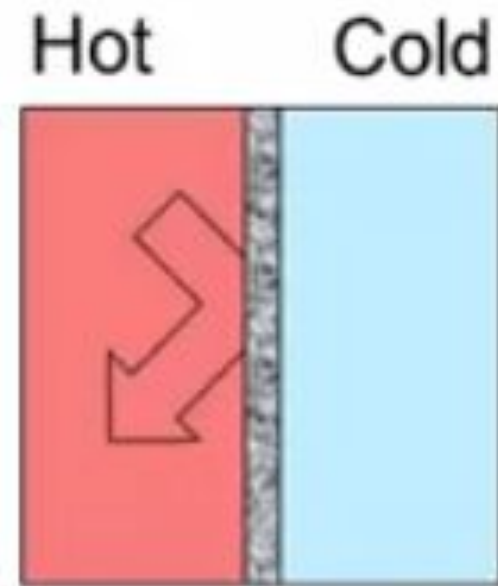- The boundary may or may not impose restrictions on such transfers.

Thermodynamic Definitions

Diathermic and Adiabatic Systems/Walls

- A diathermic system allows heat flow into or out of the system.

- An adiabatic system prevents heat flow into or out of the system.
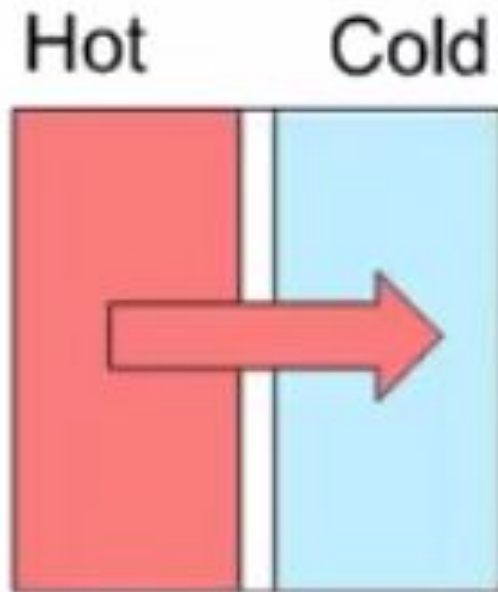
What is properties??

(1) Extensive properties

Depends on amount of matter and size of sample or systems.

Examples: mass, volume, heat capacity, no of moles and all energies term etc.

(2) Intensive properties

Does not depends on amount of matter and size of sample or systems.

Examples: Density, refractive index, Specific heat capacity, temperature, pressure, viscosity, Molarity etc.

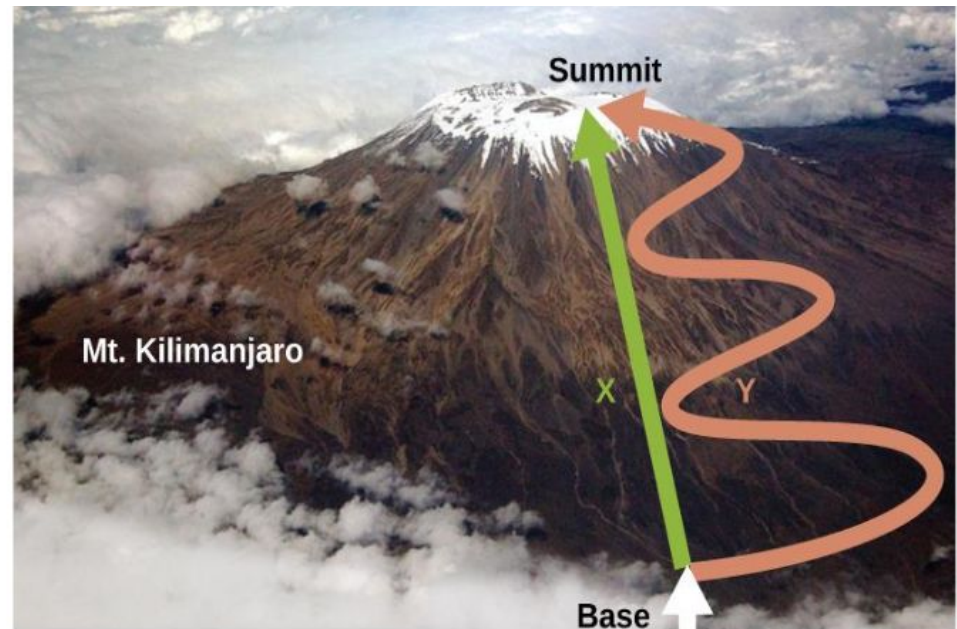**Note:** **extensive / extensive = Intensive**

Molarity = no of moles/volume

Thermodynamic Definitions

State Functions

- A state function describes the state of the system.

- The following are all state functions:
  Pressure, P;
  Volume, V;
  Temperature, T;
  Mass, m;
  Quantity, n
  Internal Energy, U;
  Enthalpy, H;
  Entropy, S;
 Gibbs Energy, G

Mt. Kilimanjaro

Thermodynamic Definitions

Path Functions

- A state function describes the current state of a system.

- How the system came to be in that particular state is of no consequence.

- Functions governing transition between the states are called path functions.

Heat (q) & Work (w): are both forms of energy. State of a system is changed by supply or removal of energy in the form of heat or work.

Random molecular motion

Energy transfer in the form of heat

Energy

Energy transfer in the form of work

Energy
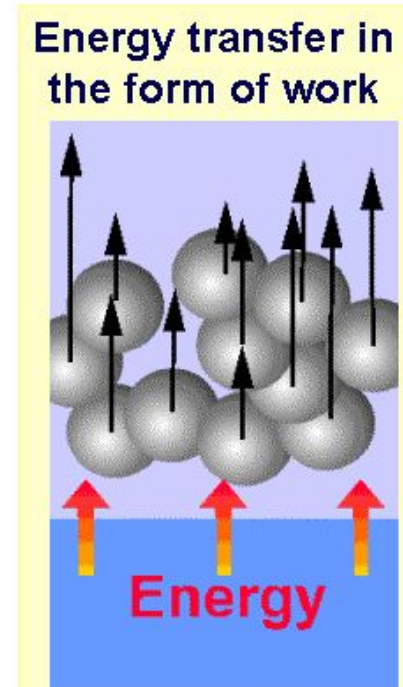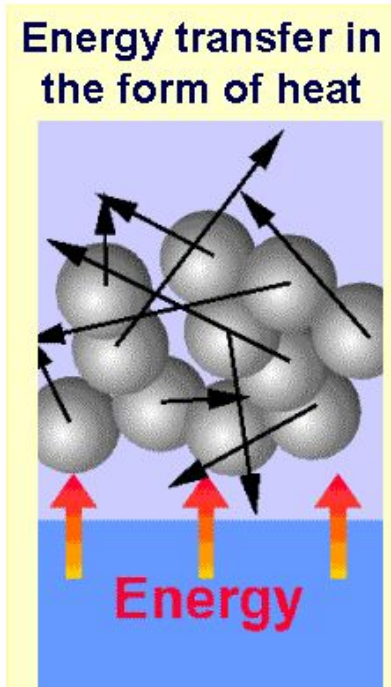
Uniform molecular motion

Isothermal, Isobaric, and Isochoric Processes

- Isothermal implies constant temperature, T.

- Isobaric implies constant pressure, P.

- Isochoric implies constant volume, V.

Laws of Thermodynamics

The Zeroth Law of Thermodynamics and Temperature

- Ironically named 0th law; last of the four laws to be discovered.

- Gives true meaning of temperature.

The First Law of Thermodynamics

- Developed around 1850 by Rudolf Clausius.

- Adaption of the Law of Conservation of Energy for Thermodynamic Systems.

- Defined change in the state function, internal energy of the system based on the energy flow into or out of the system

- Lead to the definition of a new state function called enthalpy.

Laws of Thermodynamics

The Second Law of Thermodynamics

- Developed around 1850 by Rudolf Clausius by following initial work of Sadi Carnot in 1824.

- Describes the direction in which all processes spontaneously occur, e. g. a hot object loses heat to the surroundings.

- New state function: Entropy, fundamentally measures disorder

Third Law of Thermodynamics

- Developed by German chemist Walter Nernst in 1912; While considering the behaviour of matter at absolute zero.

- Lead to the definition of zero on the entropy scale; determination of absolute entropy.
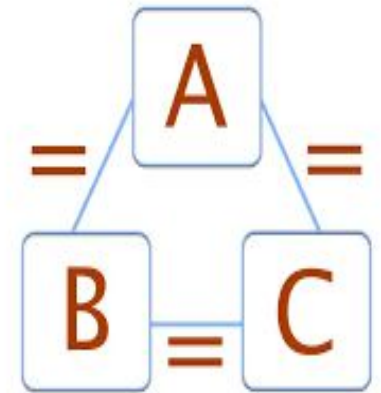
The Zeroth Law of Thermodynamics

Measurement of Temperature

- Measured routinely by a thermometer; Think how the thermometer works?

Zeroth Law

- When two objects are separately in thermodynamic equilibrium with a third object, they are in thermodynamic equilibrium with each other.

- Whenever two objects are in contact with one another, energy will flow between them until they reach a state of thermodynamic equilibrium. Upon reaching this state we say that the two objects are at the same temperature.
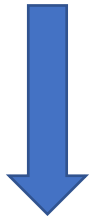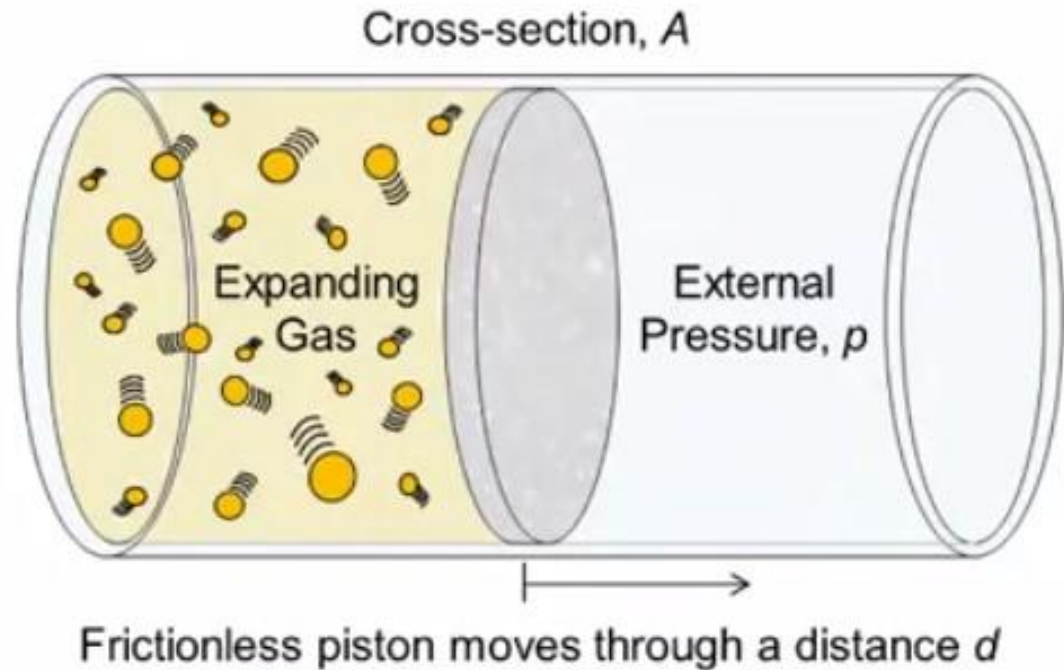
The Work Done by an Expanding gas

$$w = Fd$$

$$p = \frac{F}{A}$$

$$F = pA$$

$$w = pAd$$

$$w = p\Delta V$$

Cross-section, A

Expanding Gas

External Pressure, p

Frictionless piston moves through a distance d

$$w_{on} = -p\Delta V$$

The First Law of Thermodynamics and Enthalpy

- Law of Conservation of Energy: Energy can neither be created nor destroyed, merely changed from one form to another. Used this law for thermodynamic systems.

- Every thermodynamic system (even all matter) possesses an internal energy, U.

$$\Delta U = q_{in} + w_{on}$$

- Energy is conserved only for system + surroundings; system & surroundings can exchange energy

Chemical work done during a chemical reaction

$$Zn(s) + 2\, HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Emerging gas performs a chemical work

The First Law of Thermodynamics

$$\Delta U = q_{in} + w_{on}$$

$$w_{on} = -p\Delta V$$

$$\Delta U = q_{in} - p\Delta V$$

- Expansion work clearly depends on p and ΔV.

Free Expansion

$\Delta U = q_{in} - p\Delta V$; but in space $p = 0$ and $\Delta U = q_{in}$. However, relatively very few experiments are carried out in space.

Reactions at Constant Volume (Domain of Heavy Industries)

$\Delta U = q_{in} - p\Delta V$; but at constant volume $\Delta V = 0$ and $\Delta U = q_v$. Constant volume reactors must withstand massive pressure changes, heavy chemical industries; very expensive.
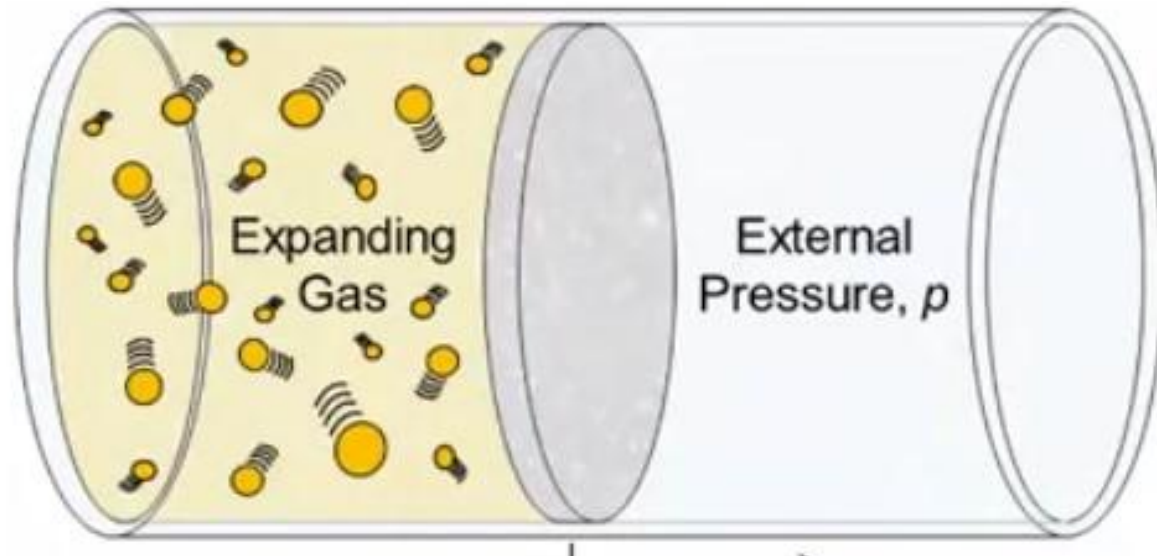
Reversible Isothermal Expansion of an Ideal Gas

❑ Leads to maximum amount of work performed by the gas.

Ideal Gas Equation: $pV = nRT$: p = Pressure; V = Volume; T = Absolute temperature measure in K; n = quantity; R = Ideal gas constant, 8.314 J K^{-1} mol^{-1}

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

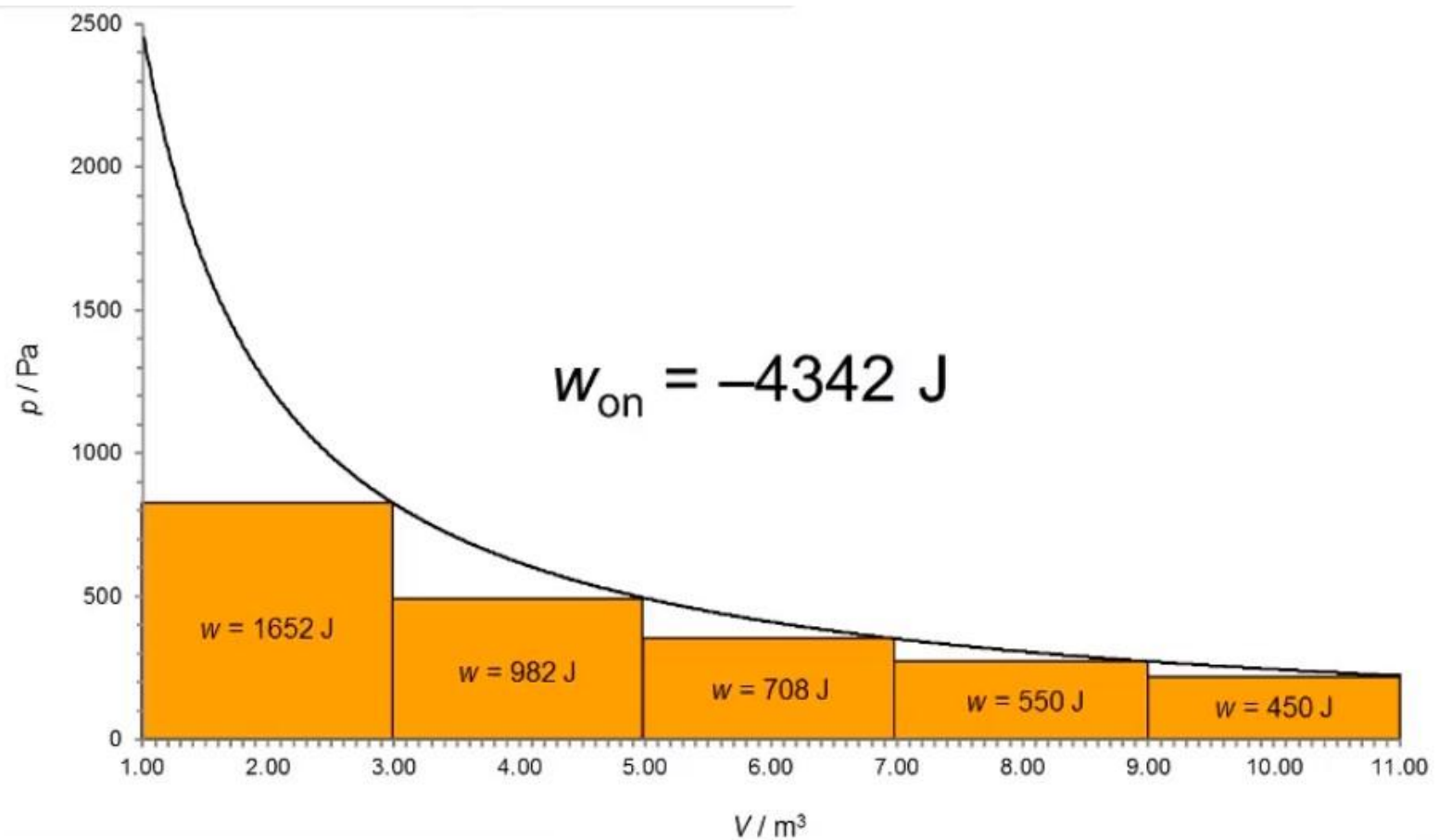# Isothermal Expansion

External pressure, p = 2478 Pa $\longrightarrow$ Volume = 1 m³.

Now imagine the gas pressure suddenly drops to 826 Pa. What happens to the gas?

Isothermal Expansion

Chart showing pressure p / Pa versus volume V / m^3 for isothermal expansion with rectangular work approximations:
- $w = 1652$ J
- $w = 982$ J
- $w = 708$ J
- $w = 550$ J
- $w = 450$ J

$W_{on} = -4342$ J
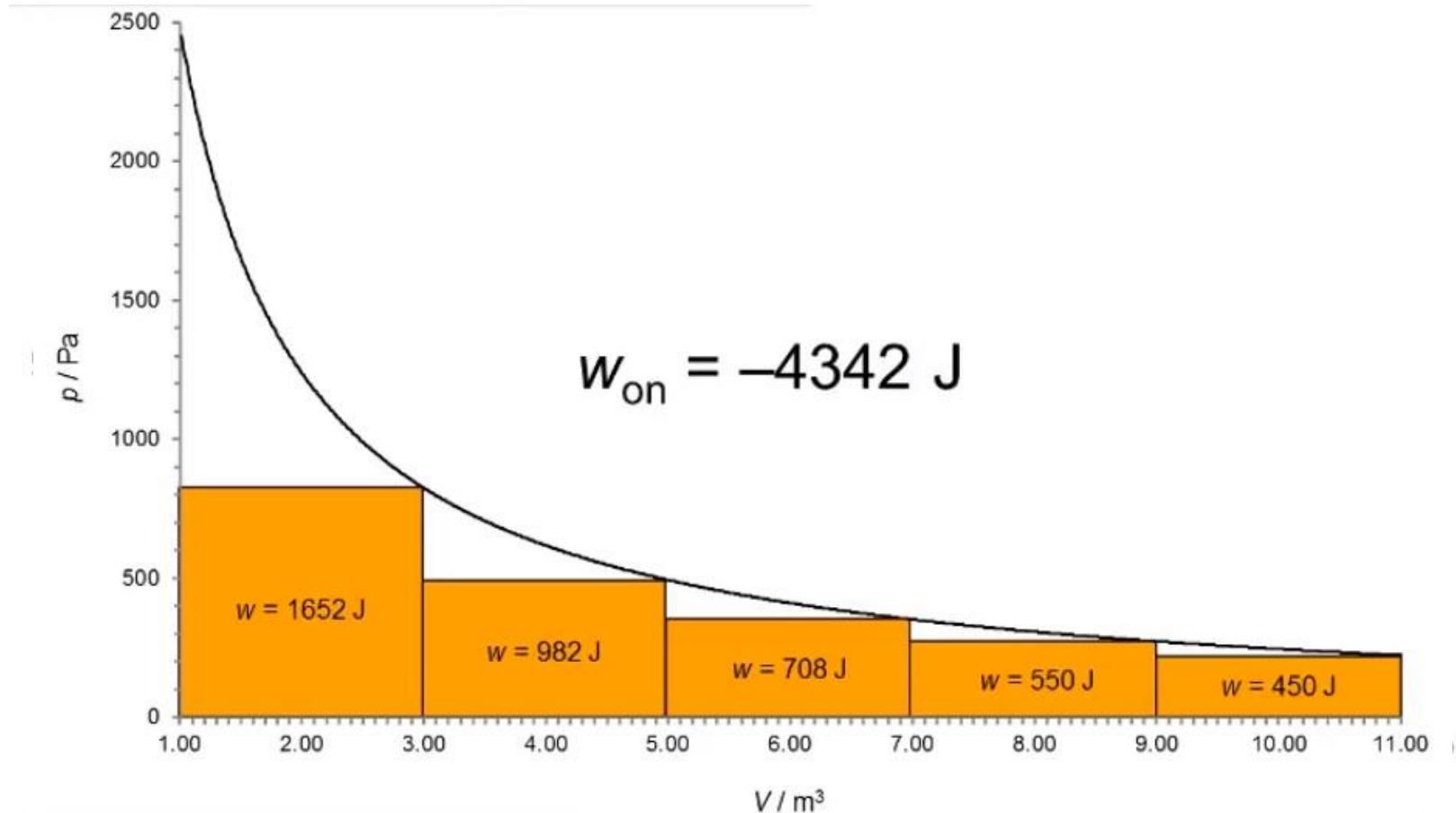
❑ Fits ideal gas equation perfectly
❑ The gas is performing work as it expands; the system is performing work: W_{on} = ??

Isothermal Expansion

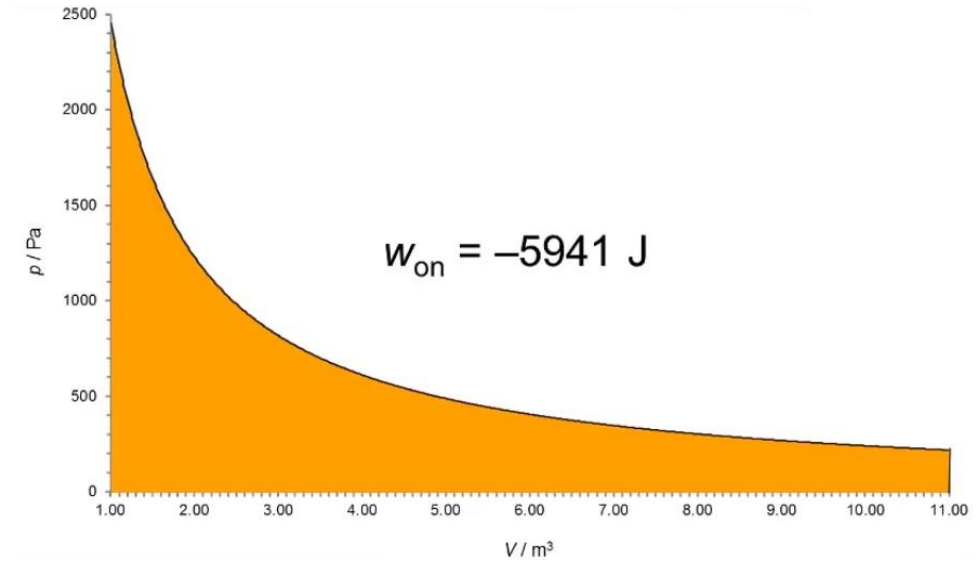❏ How to change the expansion, so that the gas performs more work?

$W_{on} = -4342$ J

w = 1652 J

w = 982 J

w = 708 J

w = 550 J

w = 450 J

w$_{on}$ for Reversible Isothermal Expansion

$$w_{on} = -pdV$$

But,

$$pV = nRT$$

So,

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

$$w_{on} = -\left(\frac{nRT}{v}\right)dV$$

$$w_{on} = -5941 \text{ J}$$

Now consider an expansion from V$_i$ to V$_f$

$$w_{on} = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$w_{on} = -nRT \ln\frac{V_f}{V_i}$$

- Reversible change is a theoretical construct.
- Determines maximum possible expansion work.

$$w_{on} = -1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln(11)$$

The First Law of Thermodynamics

Reactions at Constant Pressure (Domain of Chemists)

$\Delta U = q_{in} - p\Delta V$ ➡ $\Delta U + p\Delta V = q_{in}$ at constant pressure.

- **Now we define a new state function, enthalpy:**

$$H = U + pV$$

$\therefore \Delta H = \Delta U + \Delta(pV)$, Use product rule

$\Rightarrow \Delta H = \Delta U + p\Delta V + V\Delta p$, but at constant pressure $\Delta p = 0, V\Delta p = 0$

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

⬇

$$\Delta H = q_p$$

The First Law of Thermodynamics Does Not Predict Spontaneous Change

Limitation of 1st law of thermodynamics:

Energy is conserved. It is neither created nor destroyed, but is transferred in the form of heat and/or work.

$$\Delta E = q + w$$

The total energy of the universe is constant:

$$\Delta E_{sys} = -\Delta E_{surr} \text{ or } \Delta E_{sys} + \Delta E_{surr} = \Delta E_{univ} = 0$$

The law of conservation of energy applies to **all** changes, and does **not** allow us to predict the **direction** of a spontaneous change.

Spontaneous Change

A spontaneous change is one that occurs without a continuous input of energy from outside the system.

All chemical processes require energy (activation energy) to take place, but once a spontaneous process has begun, no further input of energy is needed.
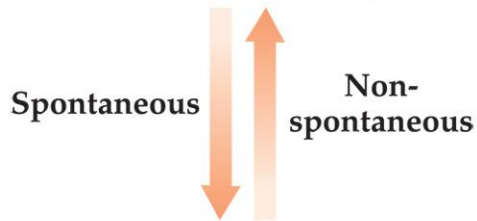
A nonspontaneous change occurs only if the surroundings continuously supply energy to the system.

If a change is spontaneous in one direction, it will be nonspontaneous in the reverse direction.
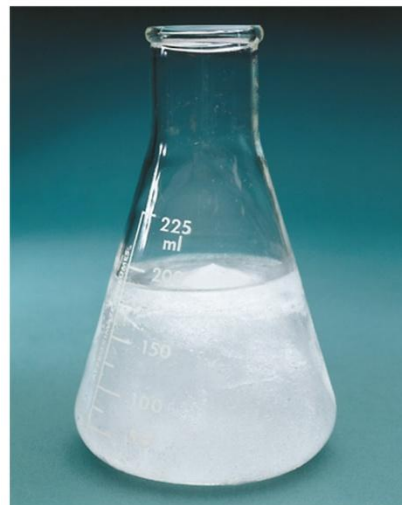
Spontaneous Processes

Spontaneous   Non-spontaneous

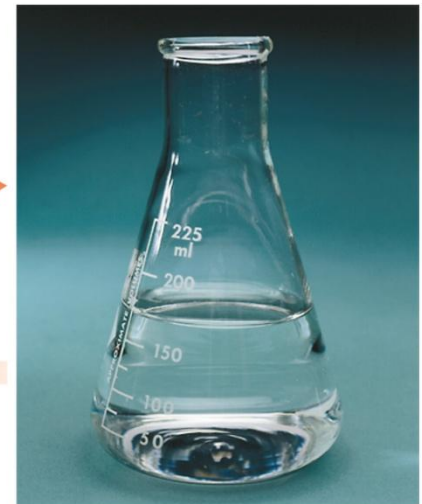Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.

Spontaneous for $T > 0°C$

Spontaneous for $T < 0°C$

ΔH Does Not Predict Spontaneous Change

A spontaneous change may be exothermic or endothermic.

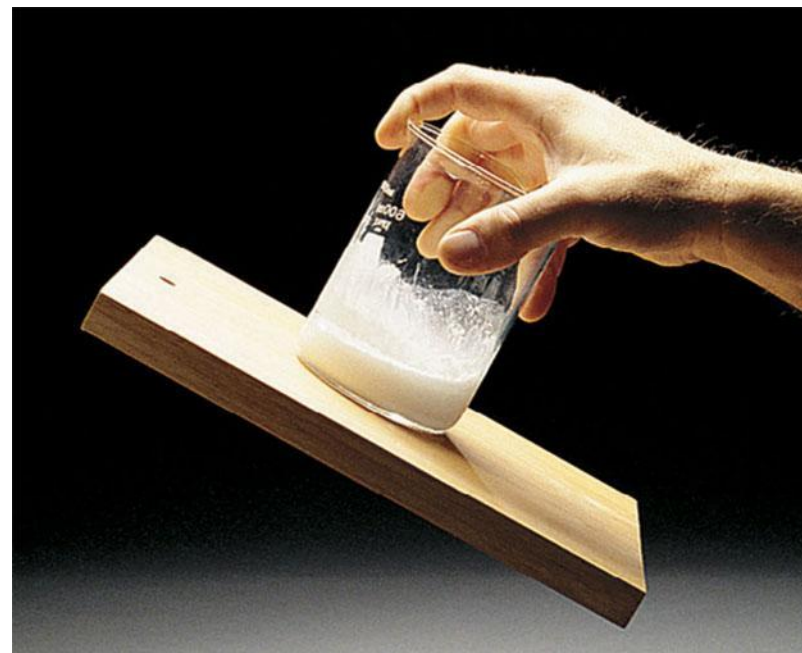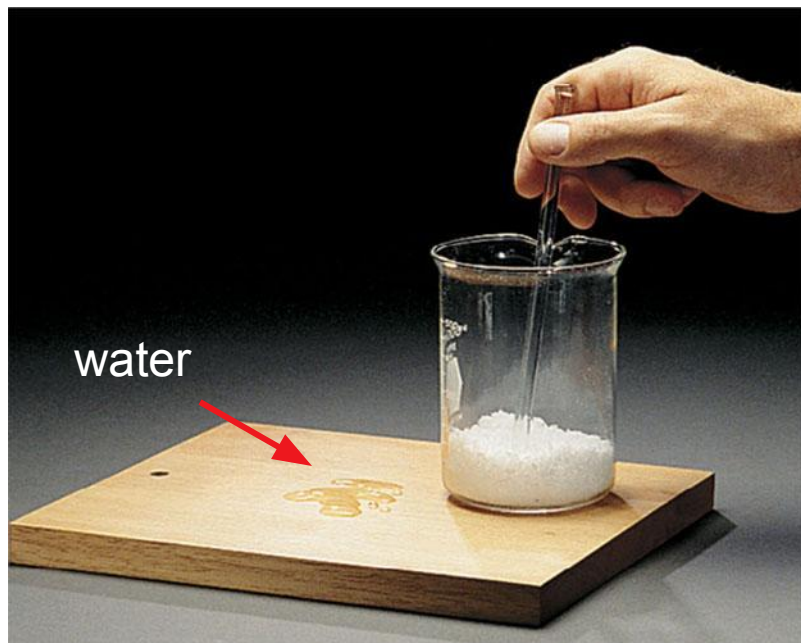Spontaneous *exothermic* processes include:
- freezing and condensation at low temperatures,
- combustion reactions,
- oxidation of iron and other metals.

Spontaneous *endothermic* processes include:
- melting and vaporization at higher temperatures,
- dissolving of most soluble salts.

The sign of ΔH does not by itself predict the direction of a spontaneous change.

A spontaneous endothermic chemical reaction.

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \rightarrow Ba^{2+}(aq) + 2NO_3^-(aq) + 2NH_3(aq) + 10H_2O(l)$$

$$\Delta H°_{rxn} = +62.3 \text{ kJ}$$
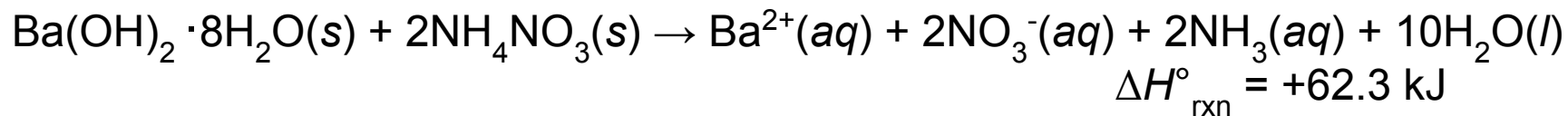
This reaction occurs spontaneously when the solids are mixed. The reaction mixture absorbs heat from the surroundings so quickly that the beaker freezes to a wet block.

Entropy

- *Entropy* (*S*) is a term coined by Rudolph Clausius in the 19th century.
- Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered,

$$\frac{q}{T}$$

- Entropy can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.

Spontaneous expansion of a gas.

A   1 mol   closed   Evacuated

B   0.5 mol   open   0.5 mol
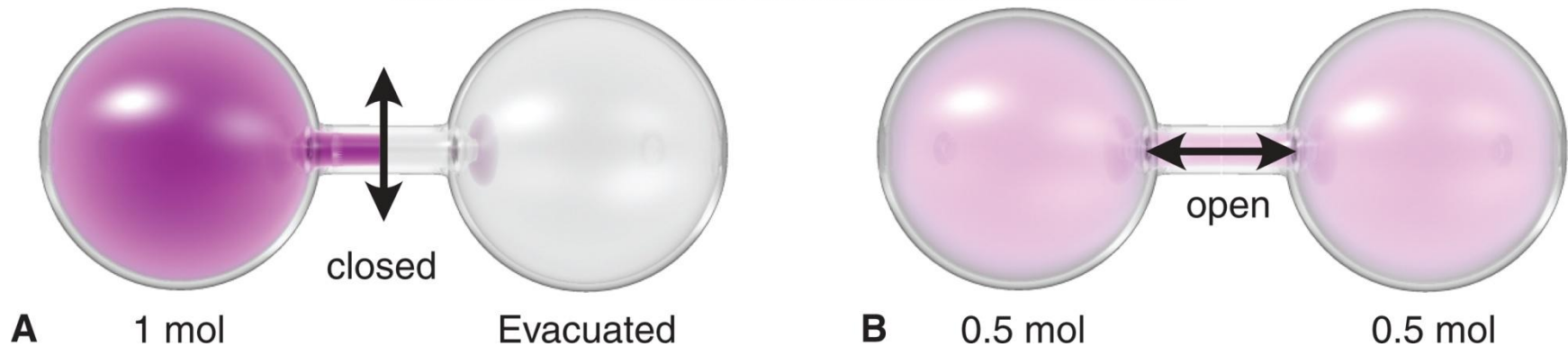
When the stopcock is opened, the gas spontaneously expands to fill both flasks.

Increasing the volume increases the number of translational energy levels the particles can occupy. The number of microstates – and the entropy – increases.

Entropy

The number of microstates (W) in a system is related to the entropy (S) of the system.

$$S = k \ln W$$

A system with fewer microstates has lower entropy.
A system with more microstates has higher entropy.

All spontaneous endothermic processes exhibit an increase in entropy.

Entropy, like enthalpy, is a state function and is therefore independent of the path taken between the final and initial states.

Microstates and Dispersal of Energy

- Just as the electronic energy levels within an atom are **quantized**, a system of particles also has different allowed energy states.

- Each quantized energy state for a system of particles is called a **microstate**.

  - At any instant, the total energy of the system is dispersed throughout one microstate.

- At a given set of conditions, each microstate has the **same** total energy as any other.

  - Each microstate is therefore equally likely.

- The larger the number of possible microstates, the larger the number of ways in which a system can disperse its energy.

Dice Sum (Macrostate)	Dice Combinations (Microstates)
2	1+1
3	1+2, 2+1
4	1+3, 2+2, 3+1
5	1+4, 2+3, 3+2, 4+1
6	1+5, 2+4, 3+3, 4+2, 5+1
7	1+6, 2+5, 3+4, 4+3, 5+2, 6+1
8	2+6, 3+5, 4+4, 5+3, 6+2
9	3+6, 4+5, 5+4, 6+3
10	4+6, 5+5, 6+4
11	5+6, 6+5
12	6+6

Expansion of a gas and the increase in number of microstates.

When the stopcock opens, the number of microstates is 2^n, where n is the number of particles.

RELATIVE NUMBER OF MICROSTATES, W
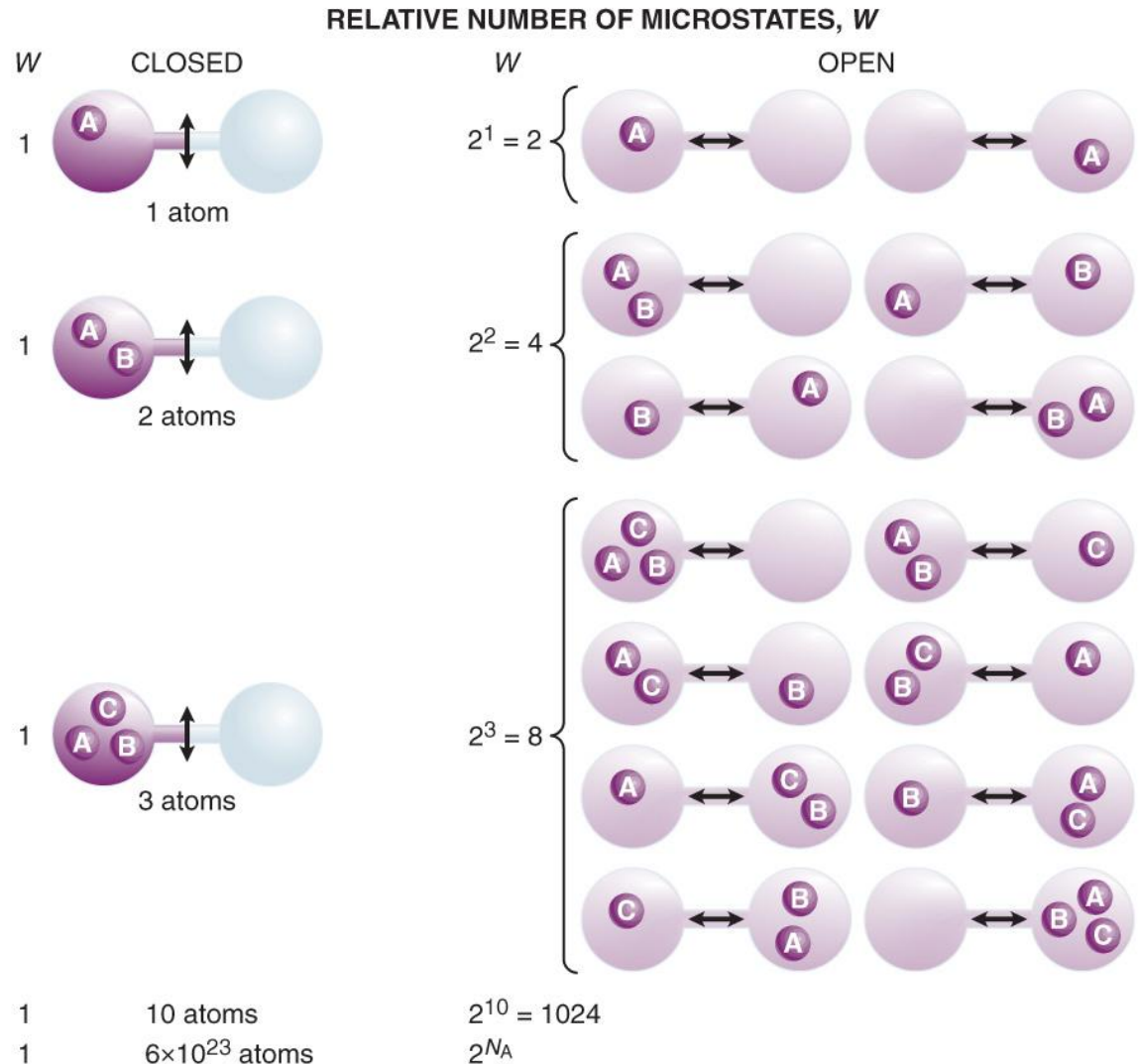
The entropy increase due to the expansion of a gas.
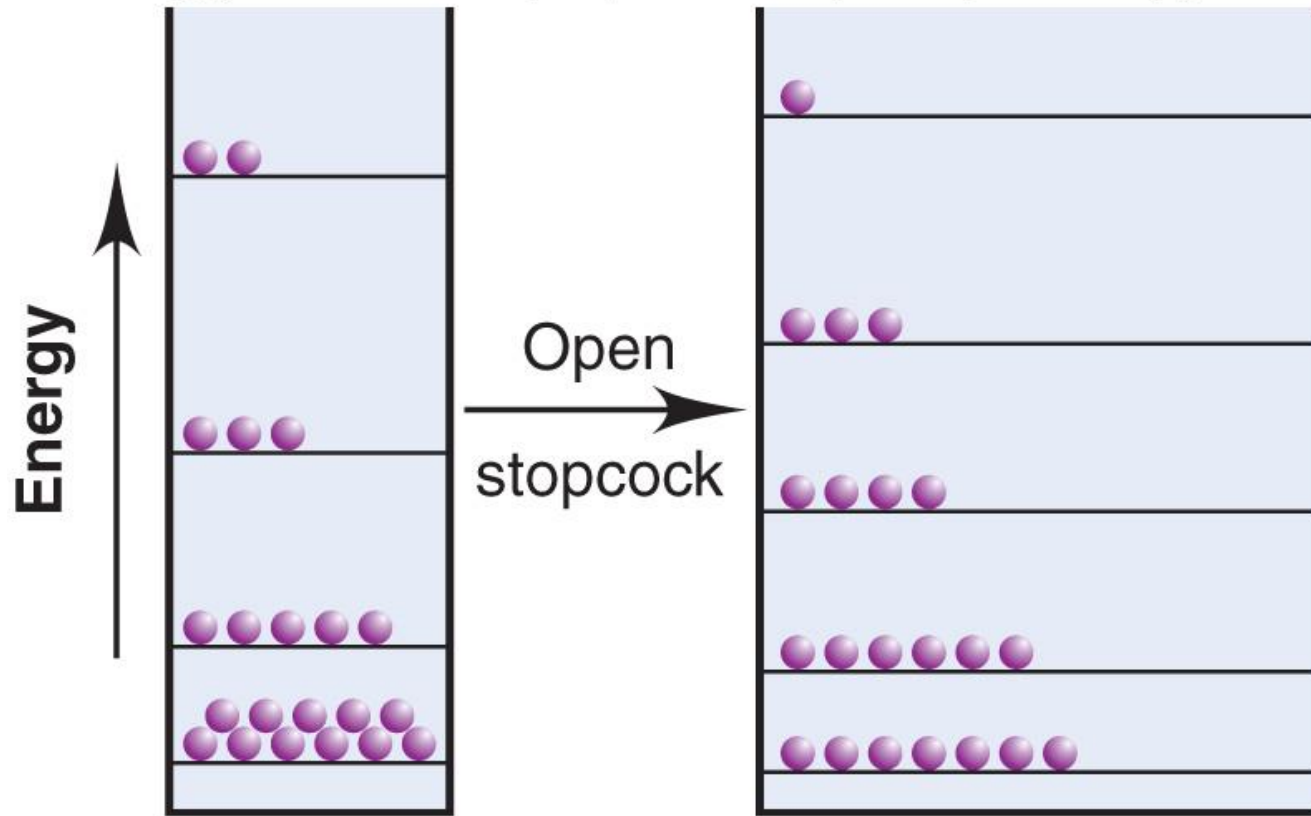
Opening the stopcock increases the number of possible energy levels, which are closer together on average. More distributions of particles are possible.

ΔS for a Reversible Process

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

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

A *reversible process* is one that occurs in such tiny increments that the system remains at equilibrium, and the direction of the change can be reversed by an infinitesimal reversal of conditions.

The Second Law of Thermodynamics

- The second law of thermodynamics says that the total entropy change of the universe must be positive for a process to be spontaneous.

  - For reversible process $\Delta S_{univ} = 0$
  - For irreversible (spontaneous) process $\Delta S_{univ} > 0$

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

- If the entropy of the system decreases, then the entropy of the surroundings must increase by a larger amount.

  - When ΔS_{system} is negative, $\Delta S_{surroundings}$ must be positive and big for a spontaneous process.
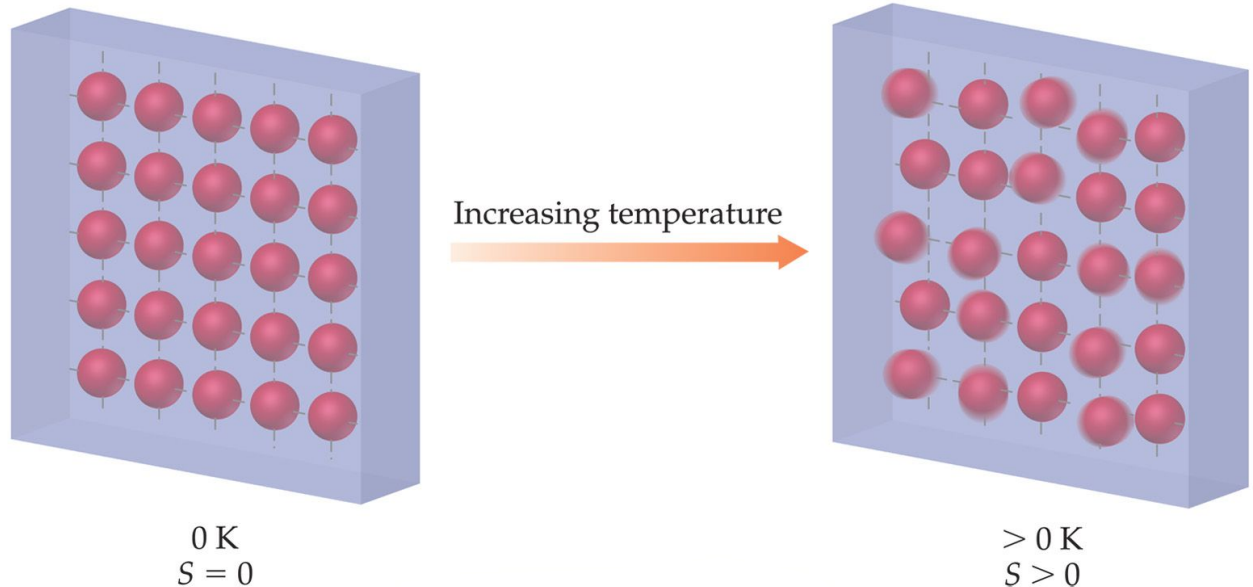
The Third Law of Thermodynamics

A perfect crystal has zero entropy at absolute zero.

$$\boxed{S_{sys} = 0 \text{ at } 0 \text{ K}}$$

A "perfect" crystal has flawless alignment of all its particles. At absolute zero, the particles have minimum energy, so there is only one microstate.

$$S = k \ln W = k \ln 1 = 0$$

Increasing temperature

0 K
S = 0

> 0 K
S > 0

Standard Molar Entropies

$S°$ is the ***standard molar entropy*** of a substance, measured for a substance in its ***standard state*** in units of J/mol·K.

The conventions for defining a standard state include:
- 1 atm for gases
- 1 *M* for solutions, and
- the pure substance in its most stable form for solids and liquids.

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K	
Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	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
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Factors Affecting Entropy

• Entropy depends on temperature.

  • For any substance, $S°$ increases as temperature increases.

• Entropy depends on the physical state of a substance.

  • $S°$ increases as the phase changes from solid to liquid to gas.

• The formation of a solution affects entropy.

• Entropy is related to atomic size and molecular complexity.

  • Remember to compare substances in the same physical state.

Visualizing the effect of temperature on entropy.

Lower T
Fewer microstates
Lower S

Higher T
More microstates
Higher S
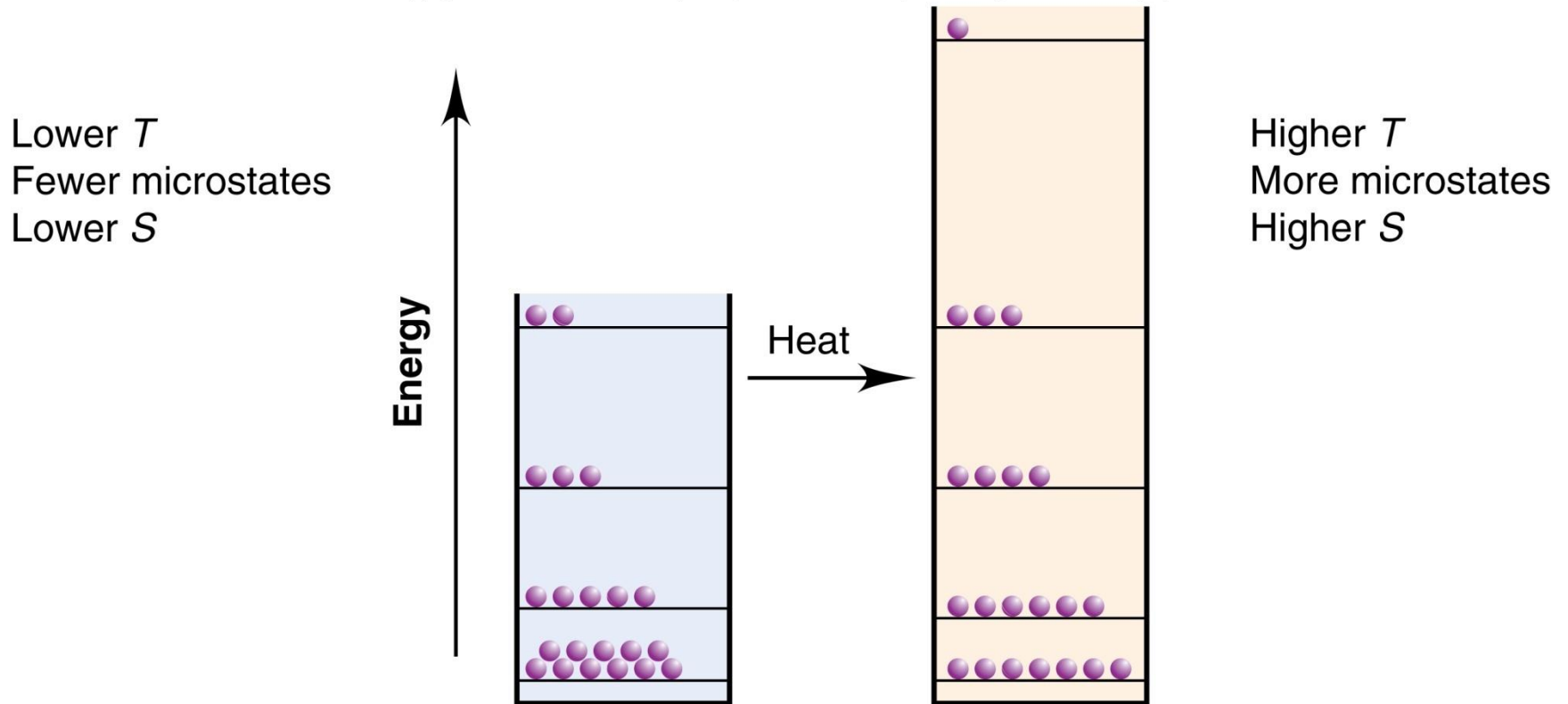
Energy

Heat

A system of 21 particles occupy energy levels (*lines*) in a box whose height represents the total energy. When heat is added, the total energy increases and becomes more dispersed, so S increases.

Visualizing the effect of temperature on entropy.

Lower T

Less freedom of motion

Fewer microstates

Lower S

Heat

Higher T

More freedom of motion

More microstates

Higher S
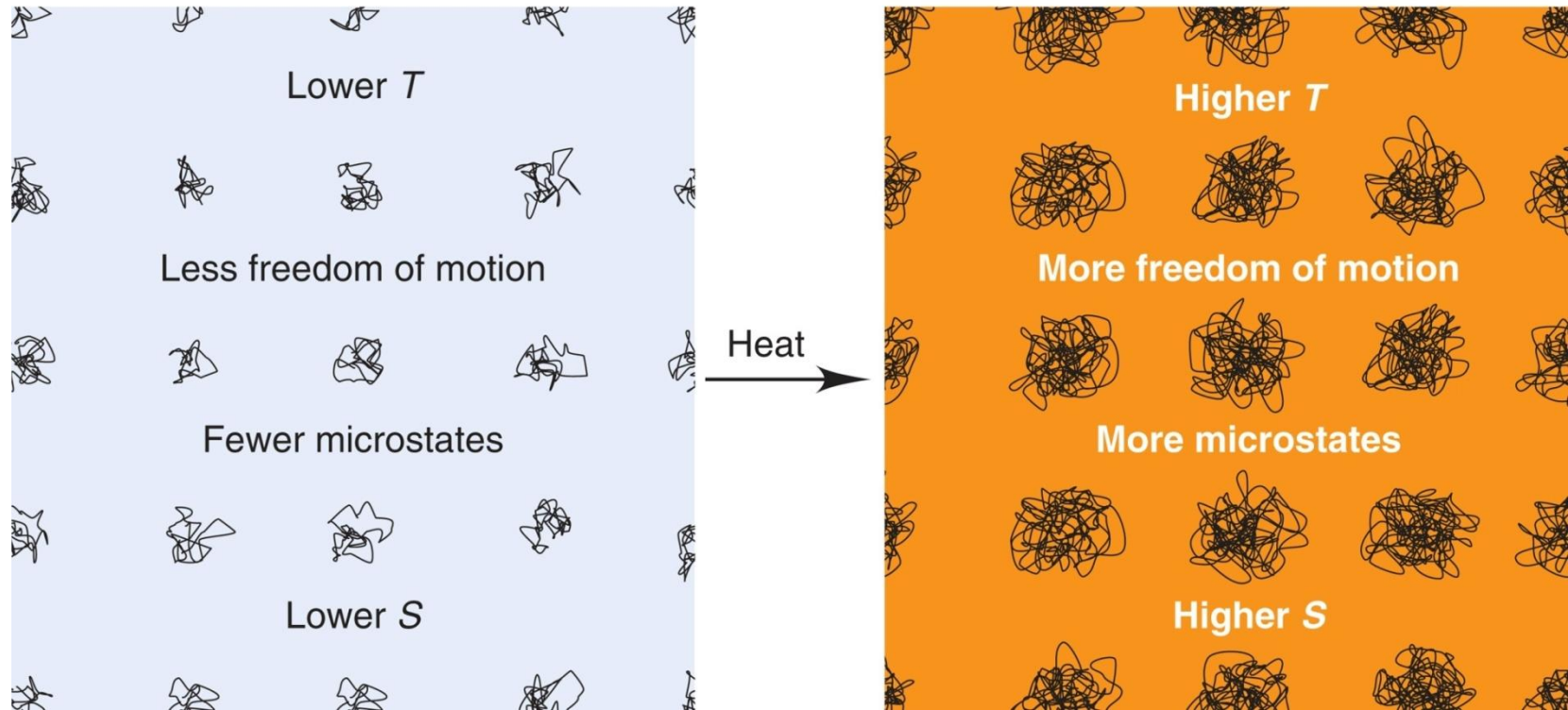
Computer simulations show each particle in a crystal moving about its lattice position. Adding heat increases T and the total energy, so the particles have greater freedom of motion, and their energy is more dispersed. S therefore increases.

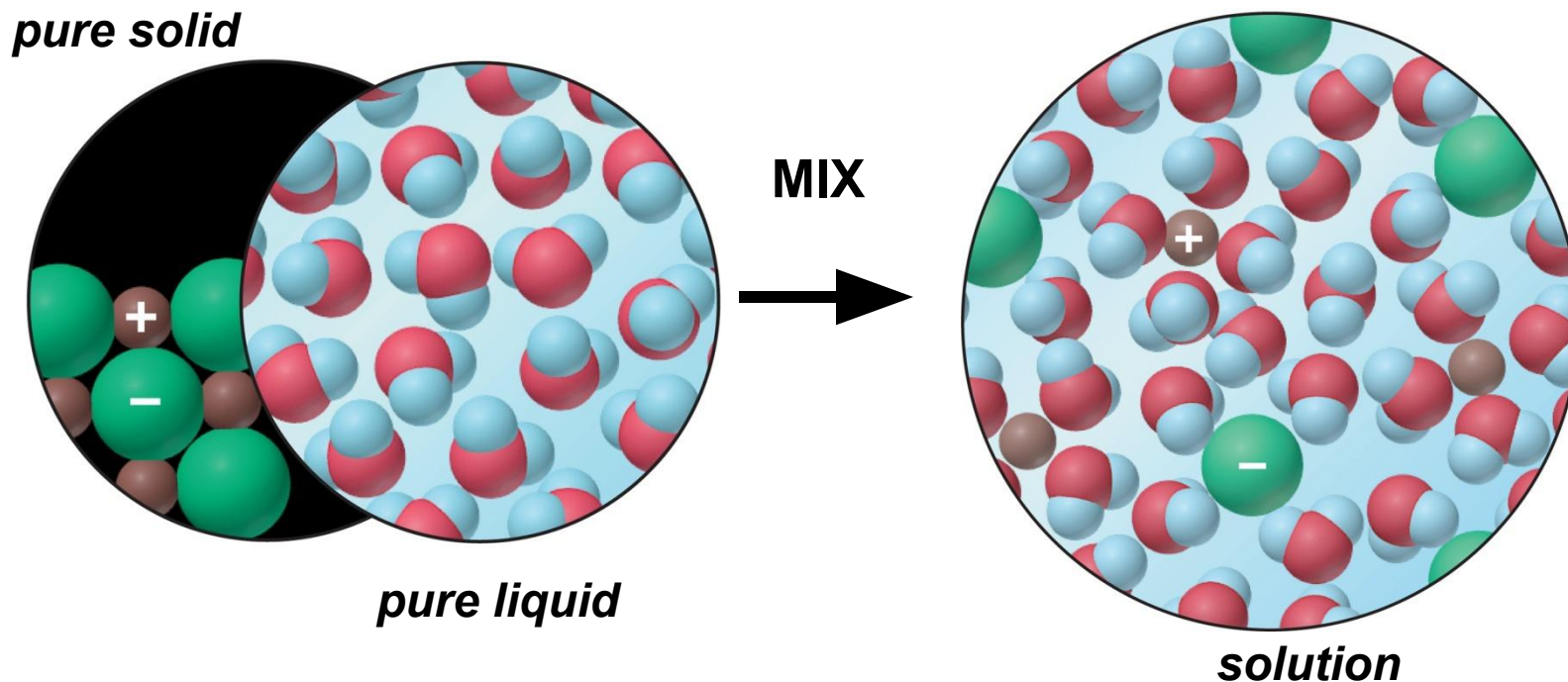# The increase in entropy during phase changes from solid to liquid to gas.
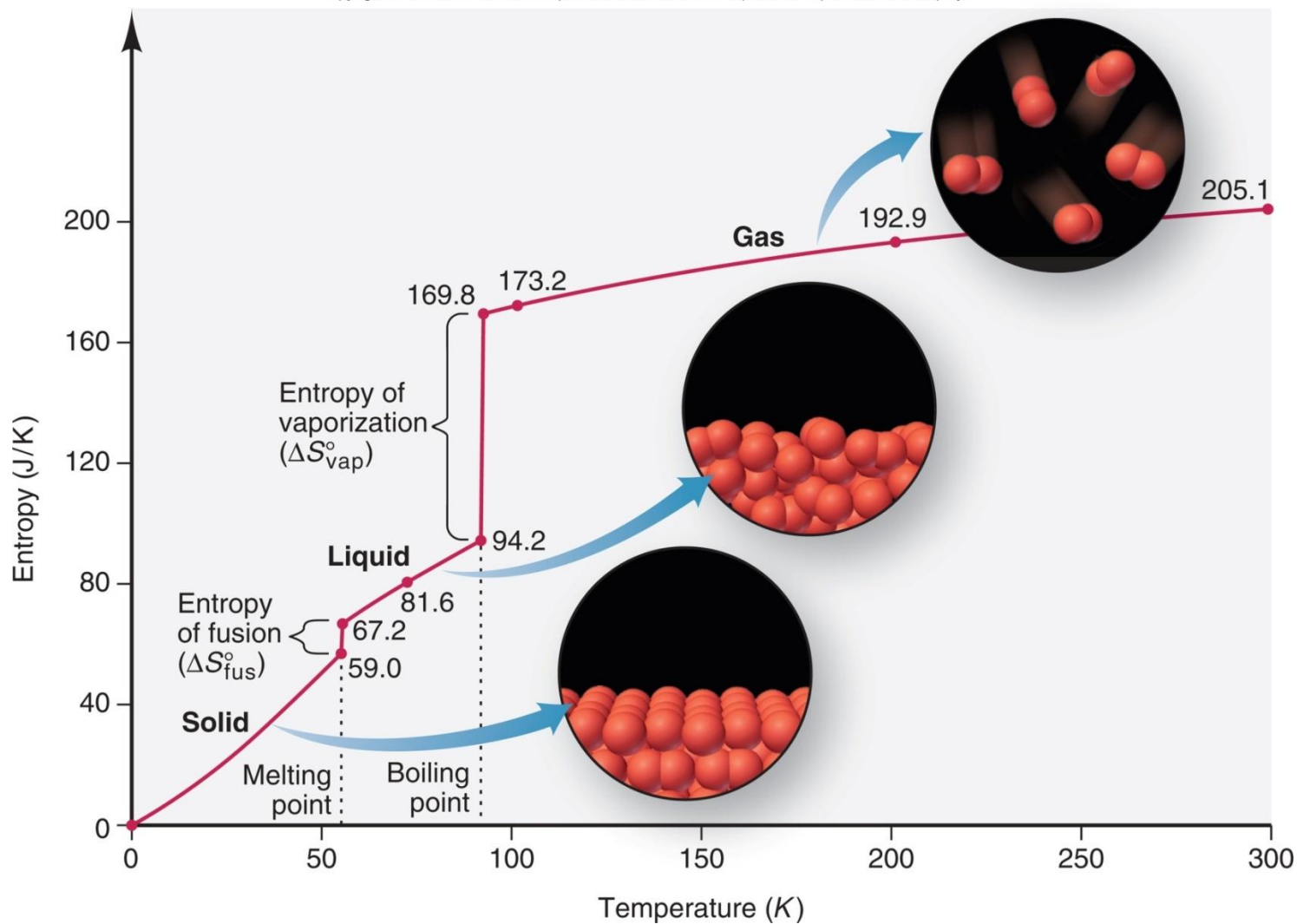
The entropy change accompanying the dissolution of a salt.

pure solid

pure liquid

MIX

solution

The entropy of a salt solution is usually ***greater*** than that of the solid and of water, but it is affected by the organization of the water molecules around each ion.

H₂O

Cl⁻ Na⁺

Hydrated Cl⁻ ion

Note the nonrandom orientation of the water molecules

Na⁺ Hydrated Na⁺ ion
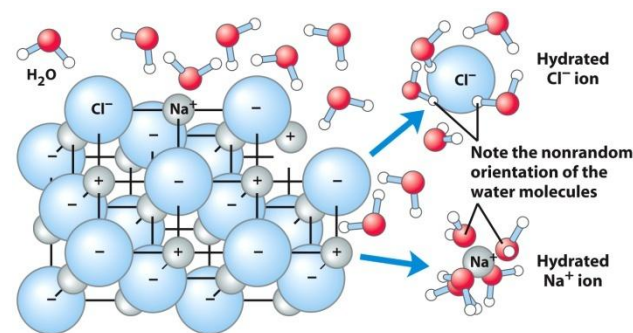
The entropy of a gas dissolved in a liquid.

Entropy of a gas is already so high that it decreases when the gas dissolves.

Entropy and Structure

For allotropes, $S°$ is higher in the form that allows the atoms more freedom of motion.

$S°$ of graphite is 5.69 J/mol·K, whereas $S°$ of diamond is 2.44 J/mol·K.

Diamond → Graphite

Diamond   Spontaneous   Graphite
           Slow rate
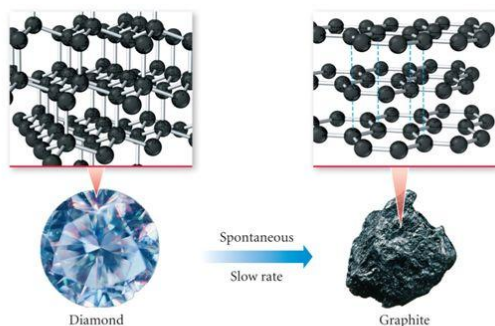
Graphite has less FE than diamond, so the conversion of diamond into graphite is spontaneous – but don't worry, it's so slow that your ring won't turn into pencil lead in your lifetime (or through many of your generations).

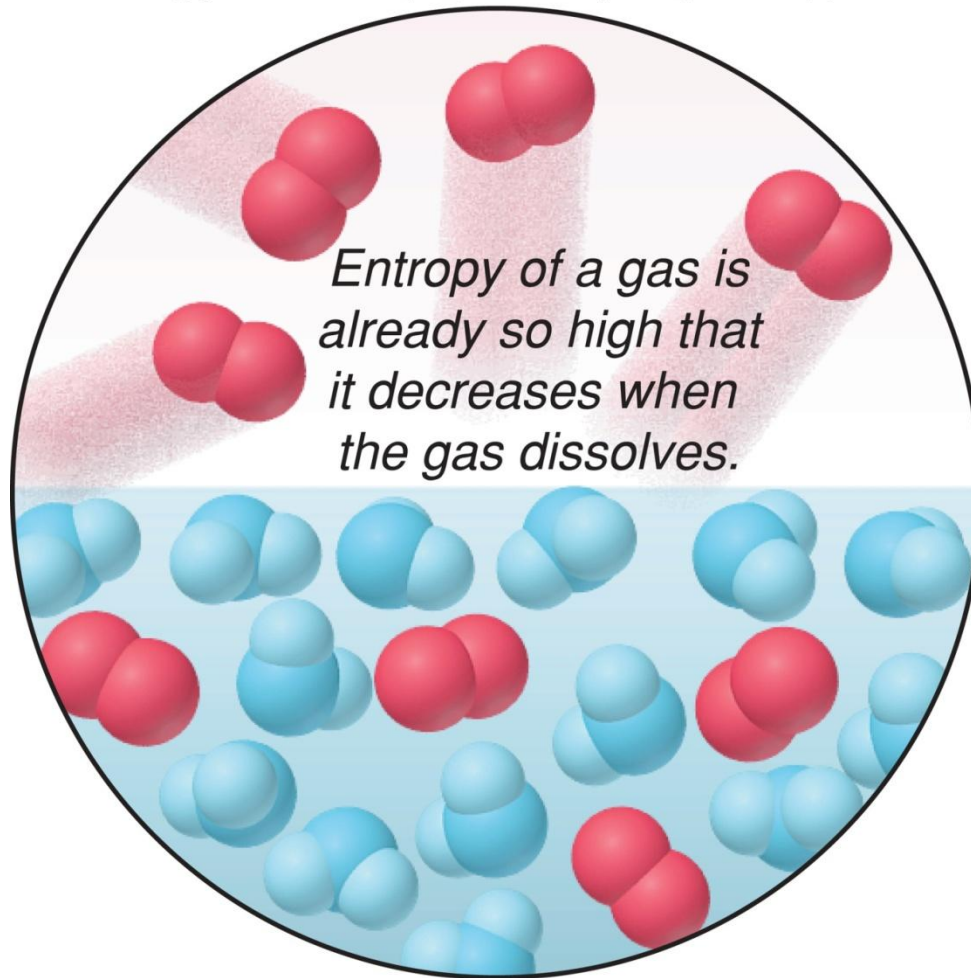Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

NO

NO_2

NO_2O_4
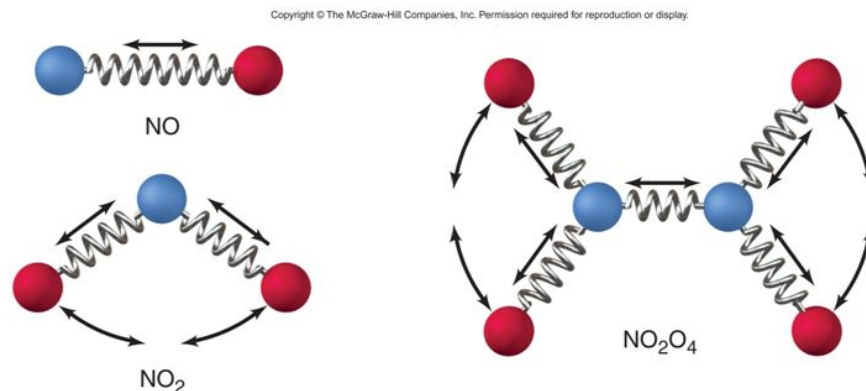
Predicting Relative Entropy Values

PROBLEM: Choose the member with the higher entropy in each of the following pairs, and justify your choice [assume constant temperature, except in part (e)]:

(a) 1 mol of $SO_2(g)$ or 1 mol of $SO_3(g)$

(b) 1 mol of $CO_2(s)$ or 1 mol of $CO_2(g)$

(c) 3 mol of $O_2(g)$ or 2 mol of $O_3(g)$

(d) 1 mol of KBr(s) or 1 mol of KBr(aq)

(e) seawater at 2°C or at 23°C

(f) 1 mol of $CF_4(g)$ or 1 mol of $CCl_4(g)$

PLAN: In general, particles with more freedom of motion have more microstates in which to disperse their kinetic energy, so they have higher entropy. Raising the temperature or having more particles increases entropy.

SOLUTION:

(a) **1 mol of $SO_3(g)$.** For equal numbers of moles of substances with the same types of atoms in the same physical state, the more atoms in the molecule the higher the entropy.

(b) **1 mol of $CO_2(g)$.** For a given substance, entropy increases as the phase changes from solid to liquid to gas.

(c) **3 mol of $O_2(g)$.** The two samples contain the same number of oxygen atoms but different numbers of molecules. Although each O_3 molecule is more complex than each O_2 molecule, the greater number of molecules dominates because there are many more microstates possible for 3 mol of particles than for 2.

(d) **1 mol of KBr(*aq*).** The two samples have the same number of ions, but their motion is more limited and their energy less dispersed in the solid than in the solution. An ionic substance in solution usually has a higher entropy than the solid.

(e) **Seawater at** 23°C. Entropy increases with rising temperature.

(f) **1 mol of $CCl_4(g)$.** For similar compounds, entropy increases with molar mass.

Entropy Changes in the System

The **standard entropy of reaction**, $\Delta S°_{rxn}$, is the entropy change that occurs when all reactants and products are in their standard states.

$$\Delta S°_{rxn} = \Sigma m S°_{products} - \Sigma n S°_{reactants}$$

where m and n are the amounts (mol) of products and reactants, given by the coefficients in the balanced equation.

Calculating the Standard Entropy of Reaction, ΔS°_{rxn}

PROBLEM: Predict the sign of ΔS°_{rxn} and calculate its value for the combustion of 1 mol of propane at 25°C.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$
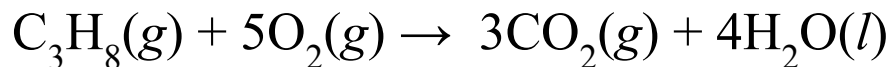
Given: S° values for C3H8, O2, CO2 and H2O are 269.9 J/K·mol, 205.0 J/K·mol, 210.0 J/K·mol and 220.0 J/K·mol respectively

PLAN: From the change in the number of moles of gas (6 mol yields 3 mol), the entropy should decrease ($\Delta S^{\circ}_{rxn} < 0$).

SOLUTION:

ΔS°_{rxn} = [(3 mol CO$_2$)(S° of CO$_2$) + (4 mol H$_2$O)(S° of H$_2$O)]
      - [(1 mol C$_3$H$_8$)(S° of C$_3$H$_8$) + (5 mol O$_2$)(S° of O$_2$)

= [(3mol)(210.0 J/K·mol) + (4 mol)(220.0 J/K·mol)]
− [(1mol)(269.9 J/K·mol) + (5 mol)(205.0 J/K·mol)   **= -216 J/K**

Entropy Changes in the Surroundings

A *decrease* in the entropy of the system is *outweighed* by an *increase* in the entropy of the surroundings.

The surroundings function as a heat source or heat sink.

In an *exothermic* process, the surroundings absorbs the heat released by the system, and S_{surr} increases.

$$q_{sys} < 0; \; q_{surr} > 0 \text{ and } \Delta S_{surr} > 0$$

In an *endothermic* process, the surroundings provides the heat absorbed by the system, and S_{surr} decreases.

$$q_{sys} > 0; \; q_{surr} < 0 \text{ and } \Delta S_{surr} < 0$$

Temperature at which Heat is Transferred

Since entropy depends on temperature, $\Delta S°_{surr}$ is also affected by the ***temperature*** at which heat is transferred.

For any reaction, $q_{sys} = -q_{surr,}$ the heat transferred is specific for the reaction and is the ***same*** regardless of the temperature of the surroundings.
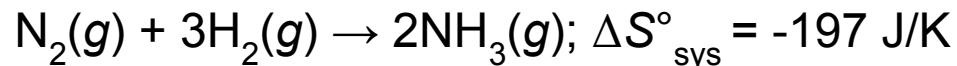
The impact on the surroundings is ***larger*** when the surroundings are at ***lower*** temperature, because there is a greater ***relative change*** in S_{surr}.

$$\Delta S_{surr} = - \frac{q_{sys}}{T}$$
$$\boxed{\Delta S_{surr} = - \frac{\Delta H_{sys}}{T}}$$ for a process at constant *P*.

Determining Reaction Spontaneity

PROBLEM: At 298 K, the formation of ammonia has a negative $\Delta S°_{sys}$;

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \Delta S°_{sys} = -197$ J/K

Calculate ΔS_{univ}, and state whether the reaction occurs spontaneously at this temperature.

SOLUTION:

$\Delta H_{rxn} = [(2 \text{ mol})(\Delta H_f \text{ of } NH_3)] - [(1 \text{ mol})(\Delta H°_f \text{ of } N_2) + (3 \text{ mol})(\Delta H_f \text{ of } H_2)]$

$= [(2 \text{ mol})(-45.9 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})]$
= - 91.8 kJ

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = -\frac{-91.8 \text{ kJ} \times \dfrac{1000 \text{ J}}{1 \text{ kJ}}}{298 \text{ K}} = 308 \text{ J/K}$$

$\Delta S°_{univ} = \Delta S°_{sys} + \Delta S°_{surr} = -197$ J/K + 308 J/K = **111 J/K**

Surroundings & system

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surround}$$

$$\Delta S_{surr} = \frac{-\Delta H^{\circ}_{sys}}{T}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H^{\circ}_{sys}}{T}$$

$$T\Delta S_{universe} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

= – Gibbs Free Energy

$$T\Delta S_{universe} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

$$\underbrace{T\Delta S_{universe}} = -\text{ Gibbs Free Energy}$$

= – Gibbs Free Energy

Make this equation nicer:

$$-T\Delta S_{universe} = \Delta H^{\circ}_{sys} - T\Delta S_{system}$$

$$\Delta G = \Delta H^{\circ}_{sys} - T\Delta S_{system}$$

Gibbs Free Energy

The Gibbs free energy (G) combines the enthalpy and entropy of a system; $G = H - TS$.

The ***free energy change*** (ΔG) is a measure of the spontaneity of a process and of the useful energy available from it.

$$\Delta G_{sys} = \Delta H_{sys} - T \Delta S_{sys}$$

$\Delta G < 0$ for a spontaneous process

$\Delta G > 0$ for a nonspontaneous process

$\Delta G = 0$ for a process at equilibrium

Calculating $\Delta G°$

$\Delta G°_{rxn}$ can be calculated using the Gibbs equation:

$$\Delta G°_{sys} = \Delta H°_{sys} - T \Delta S°_{sys}$$

$\Delta G°_{rxn}$ can also be calculated using values for the **standard free energy of formation** of the components.

$$\Delta G°_{rxn} = \Sigma m \Delta G°_{products} - \Sigma n \Delta G°_{reactants}$$

Calculating $\Delta G°_{rxn}$ from Enthalpy and Entropy Values

PROBLEM: Potassium chlorate, a common oxidizing agent in fireworks and matchheads, undergoes a solid-state disproportionation reaction when heated.

$$\overset{\textcolor{red}{+5}}{4KClO_3(s)} \xrightarrow{\Delta} \overset{\textcolor{red}{+7}}{3KClO_4(s)} + \overset{\textcolor{red}{-1}}{KCl(s)}$$

SOLUTION:

$\Delta H°_{rxn} = \Sigma m \Delta H°_{f \text{ (products)}} - \Sigma n \Delta H°_{f \text{ (reactants)}}$

$= [(3 \text{ mol } KClO_4)(\Delta H°_f \text{ of } KClO_4) + (1 \text{ mol } KCl)(\Delta H°_f \text{ of } KCl)]$

$\quad - [(4 \text{ mol } KClO_3)(\Delta H°_f \text{ of } KClO_3)]$

$= [(3 \text{ mol})(-432.8 \text{ kJ/mol}) + (1 \text{ mol})(-436.7 \text{ kJ/mol})$

$\quad - [(4 \text{ mol})(-397.7 \text{ kJ/mol})]$ **= - 144 kJ**

$\Delta S°_{rxn} = \Sigma m S°_{(products)} - \Sigma S°_{(reactants)}$

$\quad = [(3 \text{ mol of } KClO_4)(S° \text{ of } KClO_4) + (1 \text{ mol } KCl)(S° \text{ of } KCl)]$

$\quad\quad - [(4 \text{ mol } KClO_3)(S° \text{ of } KClO_3)] \quad$ **= -36.8 J/K**

$\quad = [(3 \text{ mol})(151.0 \text{ J/mol·K}) + (1 \text{ mol})(82.6 \text{ J/mol·K})$

$\quad\quad - [(4 \text{ mol})(-397.7 \text{ kJ/mol})]$

$\Delta G°_{sys} = \Delta H°_{sys} - T\,\Delta S°_{sys} = -144 \text{ kJ} - (298 \text{ K})(-36.8 \text{ J/K}) \left(\dfrac{1 \text{ kJ}}{1000 \text{ J}} \right)$
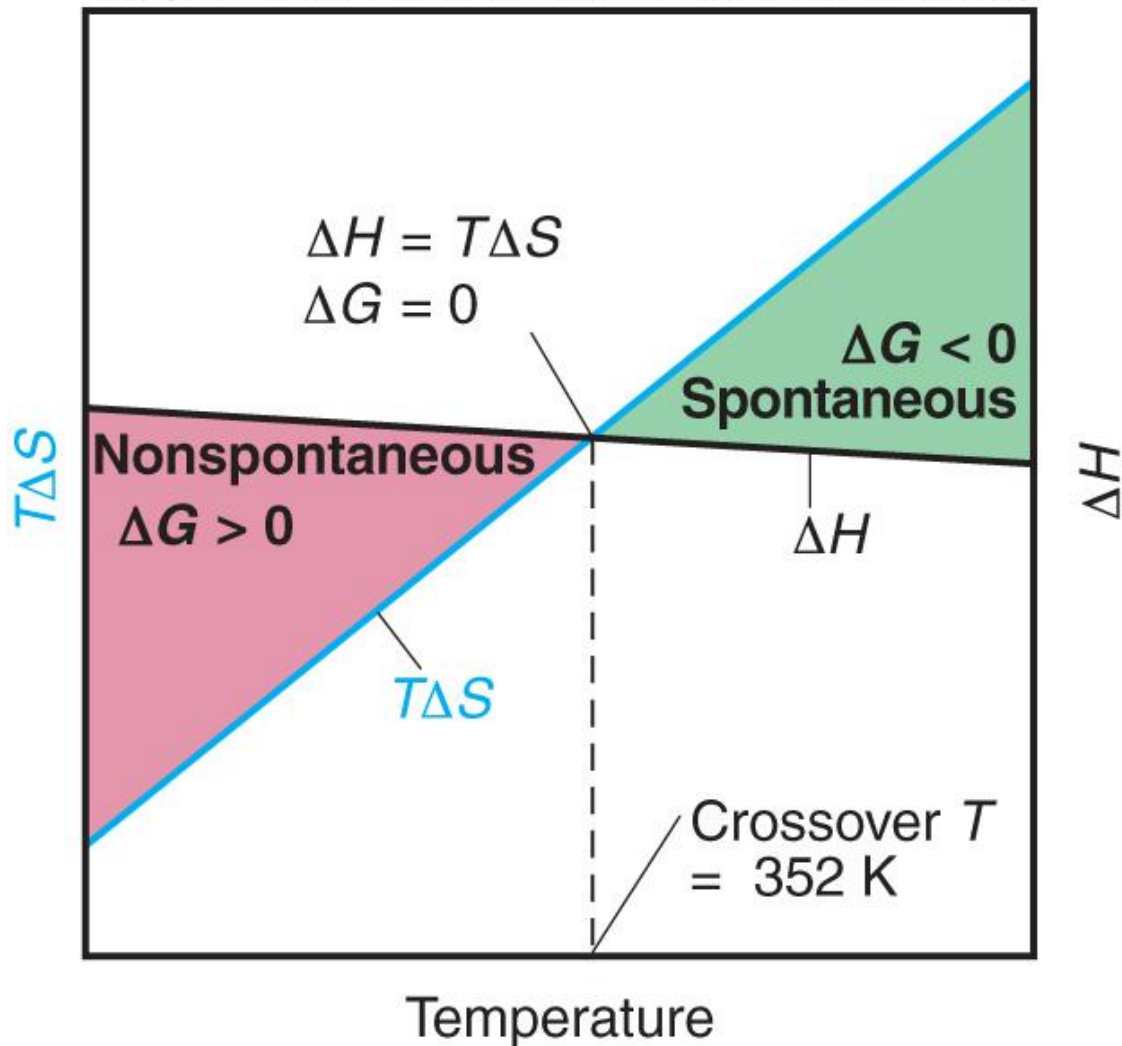
= - 134 kJ

Reaction Spontaneity and the Signs of ΔH, ΔS, and ΔG

ΔH	ΔS	$-T\Delta S$	ΔG	Description
–	+	–	–	Spontaneous at all T
+	–	+	+	Nonspontaneous at all T
+	+	–	+ or –	Spontaneous at higher T; nonspontaneous at lower T
–	–	+	+ or –	Spontaneous at lower T; nonspontaneous at higher T

The effect of temperature on reaction spontaneity.

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$\Delta H = T\Delta S$
$\Delta G = 0$

$\Delta G < 0$
Spontaneous

Nonspontaneous
$\Delta G > 0$

ΔH

$T\Delta S$

$T\Delta S$

ΔH

Crossover T = 352 K

Temperature

The sign of ΔG switches at

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

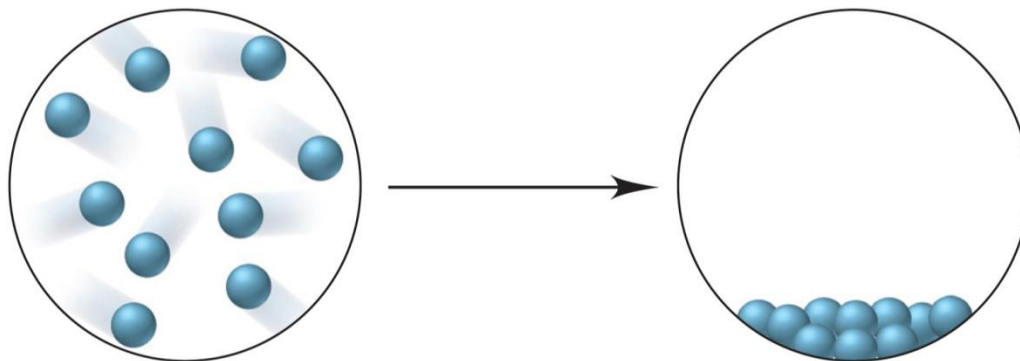# Using Molecular Scenes to Determine the Signs of ΔH, ΔS, and ΔG

PROBLEM: The following scenes represent a familiar phase change for water (*blue spheres*). Is a exothermic process.
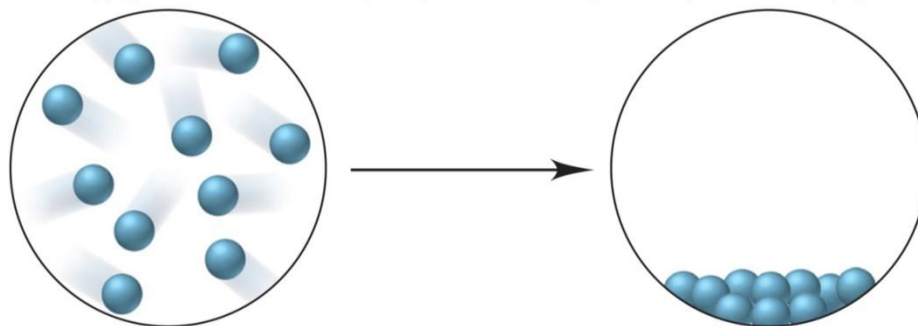
(a) What are the signs of ΔH and ΔS for this process? Explain.

(b) Is the process spontaneous at all T, no T, low T, or high T? Explain.

SOLUTION:

(a) The scene represents the condensation of water vapor, so the amount of gas decreases dramatically, and the separated molecules give up energy as they come closer together.

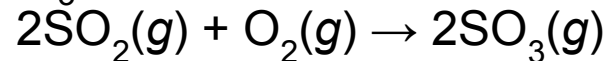$$\Delta S < 0 \text{ and } \Delta H < 0$$

(b) Since ΔS is negative and T is constant, the $-T\Delta S$ term is positive. In order for ΔG to be < 0, the temperature must be low.

The process is spontaneous at low temperatures.

Determining the Effect of Temperature on ΔG

PROBLEM: A key step in the production of sulfuric acid is the oxidation of $SO_2(g)$ to $SO_3(g)$:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

At 298 K, ΔG = -141.6 kJ; ΔH = -198.4 kJ; and ΔS = -187.9 J/K

(a) Use the data to decide if this reaction is spontaneous at 25°C, and predict how ΔG will change with increasing T.

(b) Assuming ΔH and ΔS are constant with increasing T, is the reaction spontaneous at 900°C?

SOLUTION:

(a) $\Delta G < 0$ at 209 K (= 25°C), so **the reaction is spontaneous**.

With $\Delta S < 0$, the term $-T\Delta S > 0$ and this term will become more positive at higher T.

ΔG will become less negative, and the reaction less spontaneous, with increasing T.

(b) $\Delta G = \Delta H - T\Delta S$

Convert T to K: 900. + 273.15 = 1173 K
Convert S to kJ/K: -187.9 J/K = 0.1879 kJ/K

ΔG = -198.4 kJ – [1173 K)(-0.187.9 kJ/K) = **22.0 kJ**

$\Delta G > 0$, so the reaction is nonspontaneous at 900°C.

Free Energy and Equilibrium

$$\Delta G = RT \ln \frac{Q}{K} = RT \ln Q - RT \ln K$$

If Q and K are very different, ΔG has a very large value (positive or negative). The reaction releases or absorbs a large amount of free energy.

If Q and K are nearly the same, ΔG has a very small value (positive or negative). The reaction releases or absorbs very little free energy.

For standard state conditions, $Q = 1$ and $\quad \Delta G° = -RT \ln K$

To calculate ΔG for any conditions:

$$\Delta G = \Delta G° + RT \ln Q$$

$\Delta G°$ and Useful Work

ΔG is the **_maximum useful work_** done **_by_** a system during a **_spontaneous_** process at constant T and P.
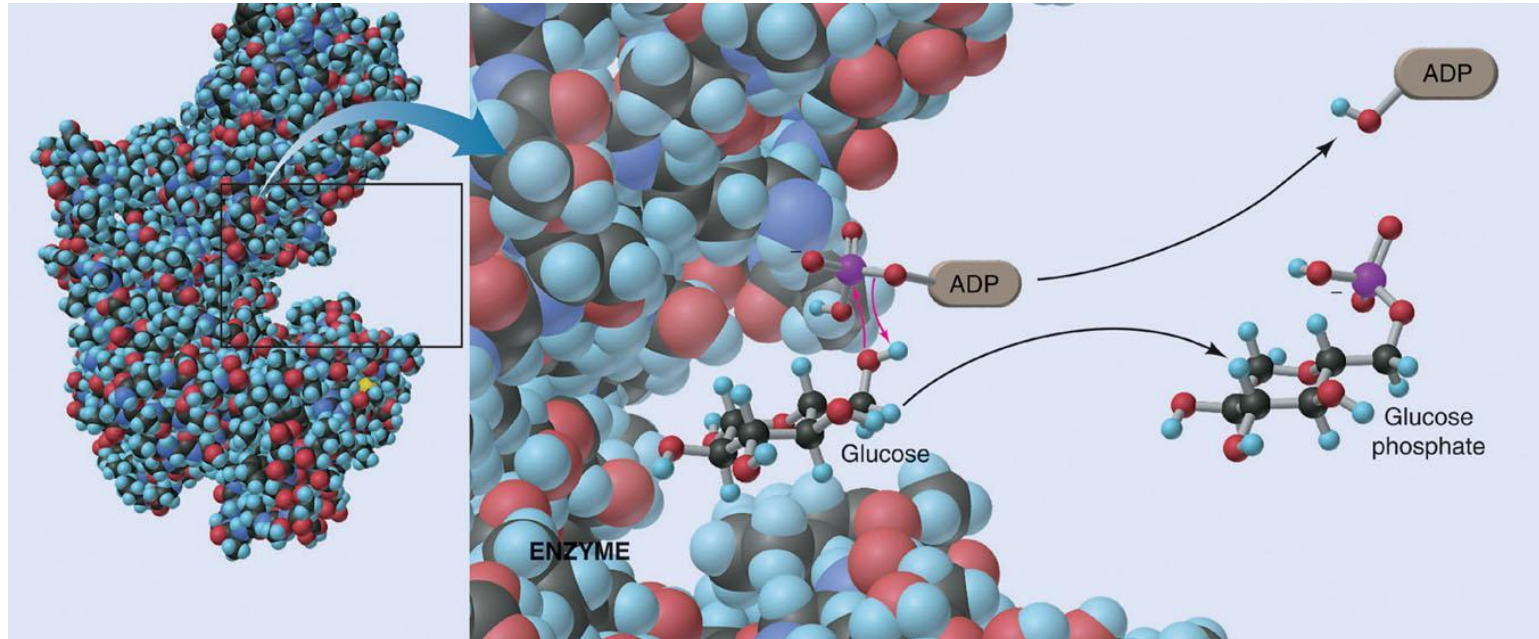
In practice, the maximum work is never done. Free energy not used for work is lost to the surroundings as heat.

ΔG is the **_minimum work_** that must be done **_to_** a system to make a **_nonspontaneous_** process occur at constant T and P.

A reaction at equilibrium ($\Delta G_{sys} = 0$) can no longer do any work.

Chemical Connections

The coupling of a nonspontaneous reaction to the hydrolysis of ATP.

A spontaneous reaction can be coupled to a nonspontaneous reaction so that the spontaneous process provides the free energy required to drive the nonspontaneous process. The coupled processes must be physically connected.

Chemical Connections

The cycling of metabolic free energy.