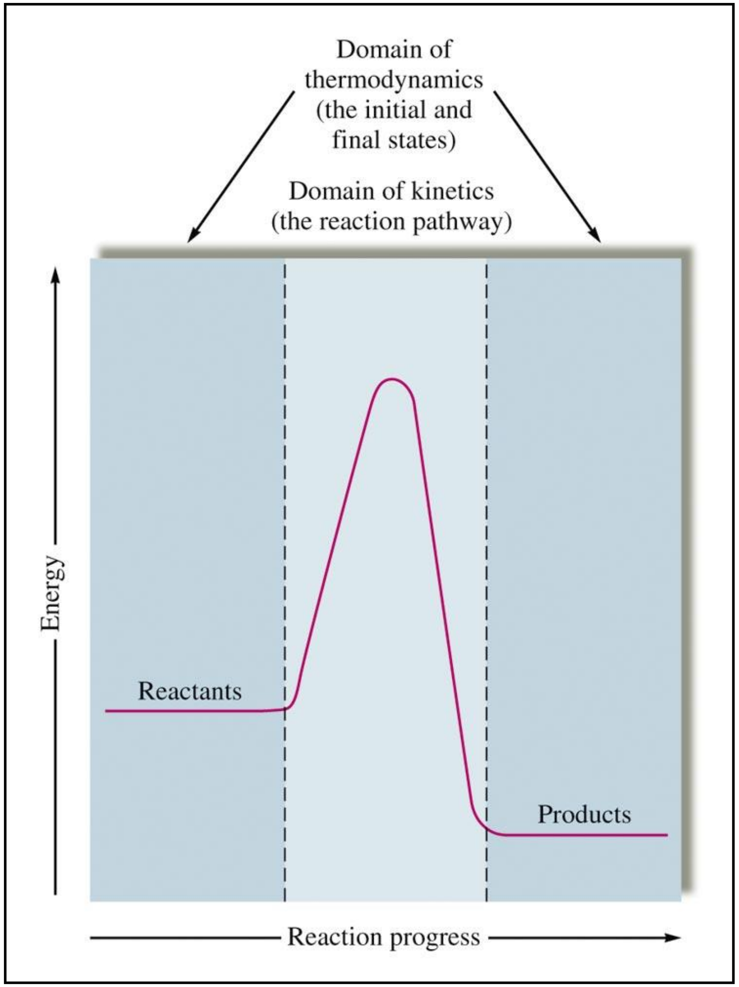
Chemical Thermodynamics

- The chemistry that deals with energy exchange, entropy, and the spontaneity of a chemical process.

Thermodynamics vs. Kinetics

- Kinetics Domain
    - Rate of a reaction depends on the pathway from reactants to products.
- Thermodynamics tells us whether a reaction is spontaneous based only on the properties of reactants and products.


Domain of thermodynamics (the initial and final states)
Domain of kinetics (the reaction pathway)
Energy
Reactants
Products
Reaction progress

First Law of Thermodynamics

- The change in the *internal energy* (ΔE) of a thermodynamic system is equal to the amount of *heat energy* (q) added to or lost by the system plus *work done* (w) on or by the system.

$$\Delta E = q + w$$

- For *work* that only involves gas expansion or compression, $w = -p\Delta V$;

Values of Thermodynamic Functions

- FLoT: $\Delta E = q + w$;
  - q is assigned a *positive* value if *heat is absorbed*, but a *negative* value if *heat is lost* by the system;
  - w is assigned a *positive* value if *work is done on*, but a *negative* value if *work is done by* the system.
  - For processes that do not involve phase changes, positive ΔE results in temperature increase.

Spontaneous Processes and Entropy

- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.

Concept Check

Consider 2.4 moles of a gas contained in a 4.0 L bulb at a constant temperature of 32°C. This bulb is connected by a valve to an evacuated 20.0 L bulb. Assume the temperature is constant.

a) What should happen to the gas when you open the valve?

Concept Check

Consider 2.4 moles of a gas contained in a 4.0 L bulb at a constant temperature of 32°C. This bulb is connected by a valve to an evacuated 20.0 L bulb. Assume the temperature is constant.

b) Calculate ΔH, ΔE, q, and w for the process you described above.

All are equal to zero.

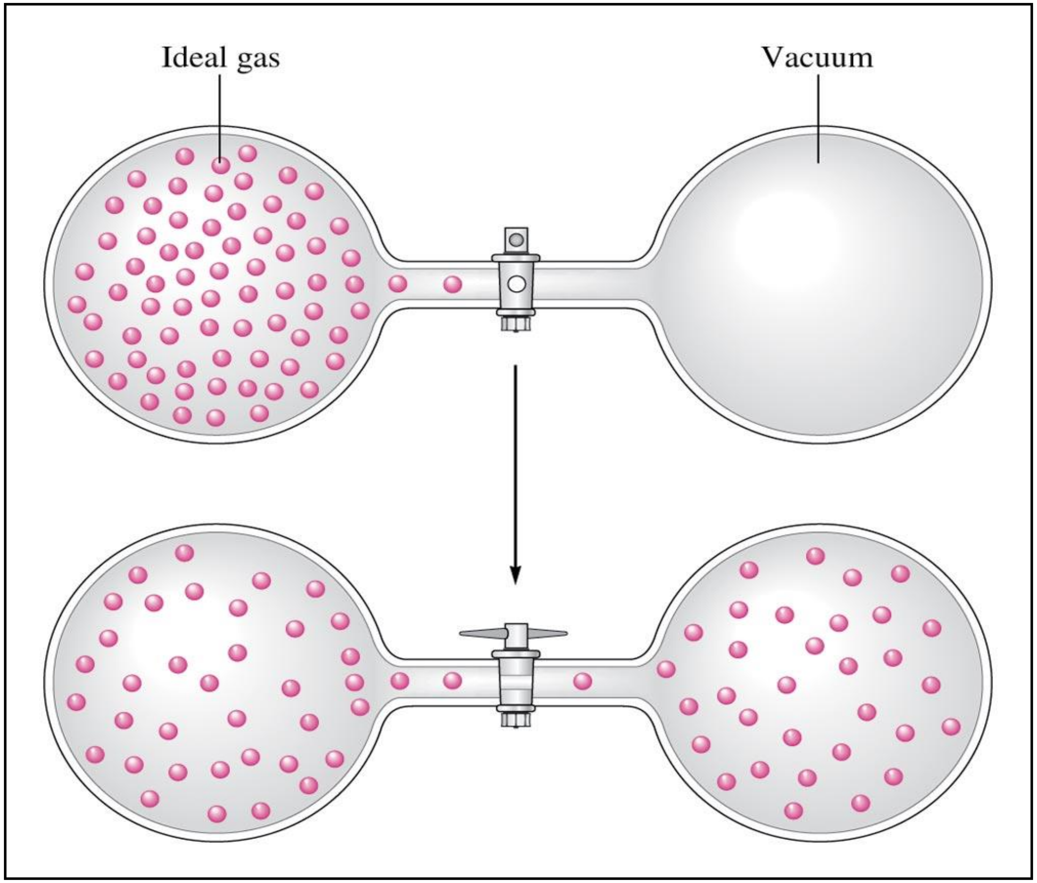
Concept Check

Consider 2.4 moles of a gas contained in a 4.0 L bulb at a constant temperature of 32°C. This bulb is connected by a valve to an evacuated 20.0 L bulb. Assume the temperature is constant.

c) Given your answer to part b, what is the driving force for the process?

Entropy

The Expansion of An Ideal Gas Into an Evacuated Bulb


Ideal gas
Vacuum

Entropy

- Thermodynamic function that describes the number of arrangements that are available to a system existing in a given state.

What is Entropy?

- A thermodynamic (*energy*) function that describes the degree of ***randomness*** or ***probability*** of existence.
- As a *state function* – entropy change depends only on the initial and final states, but not on how the change occurs.

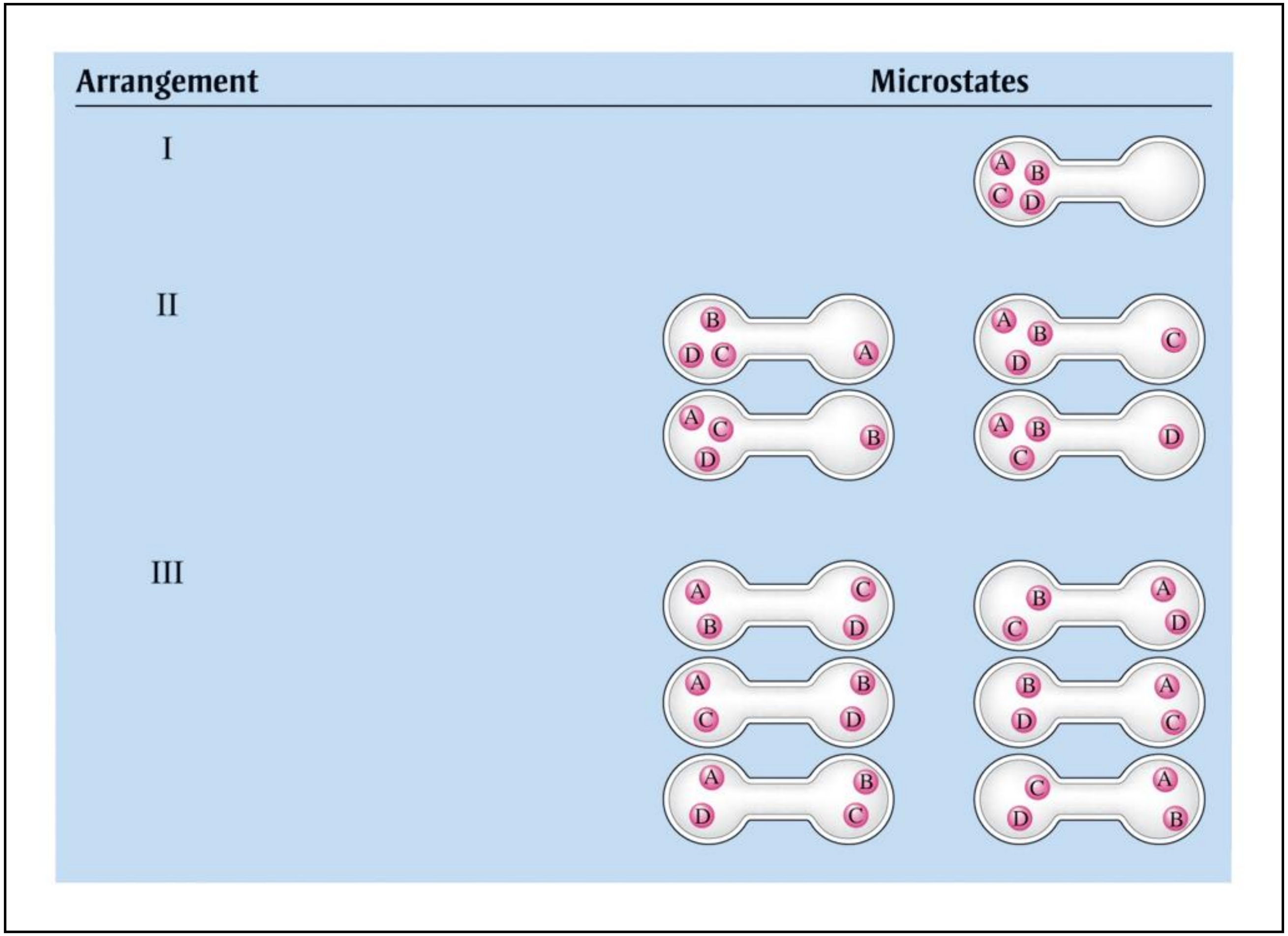
Entropy

- The driving force for a spontaneous process is an increase in the entropy of the universe.

What is the significance of *entropy*?

- Nature spontaneously proceeds toward the state that has the highest probability of (energy) existence – highest entropy
- Entropy is used to predict whether a given process/reaction is thermodynamically possible;

The Microstates That Give a Particular Arrangement (State)


Arrangement
Microstates
I
II
III

The Microstates That Give a Particular Arrangement (State)

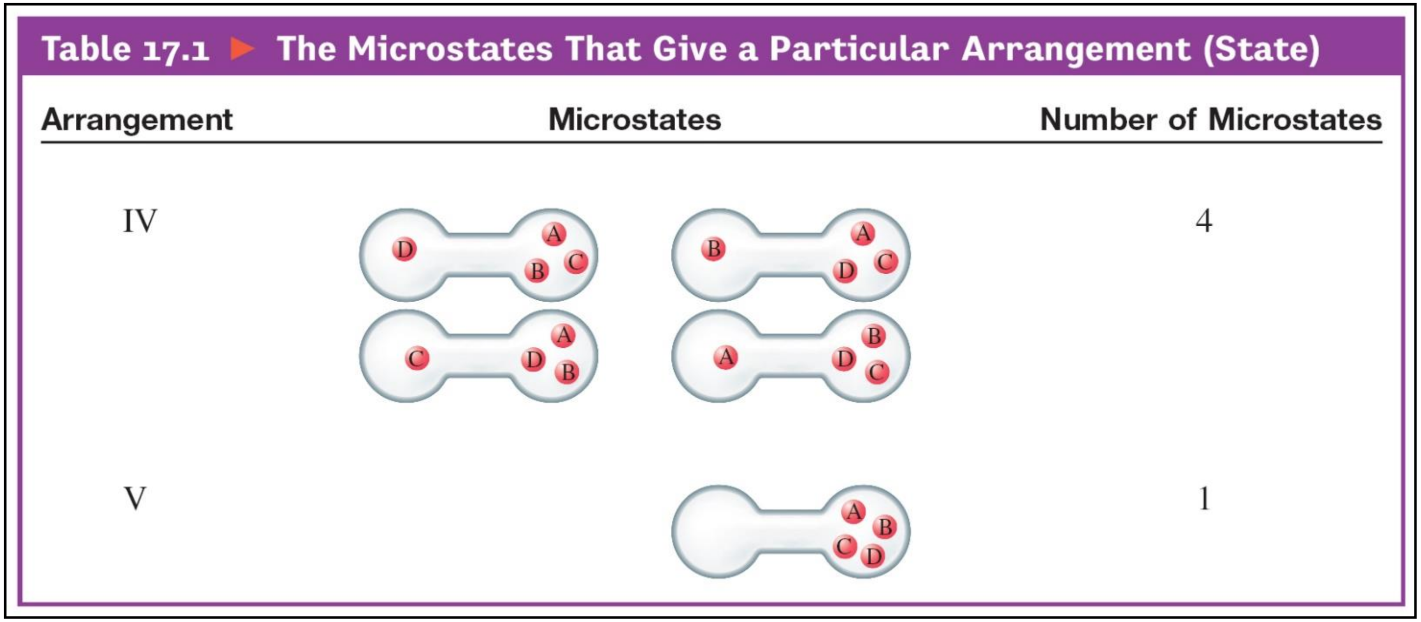


Table 17.1 ▶ The Microstates That Give a Particular Arrangement (State)

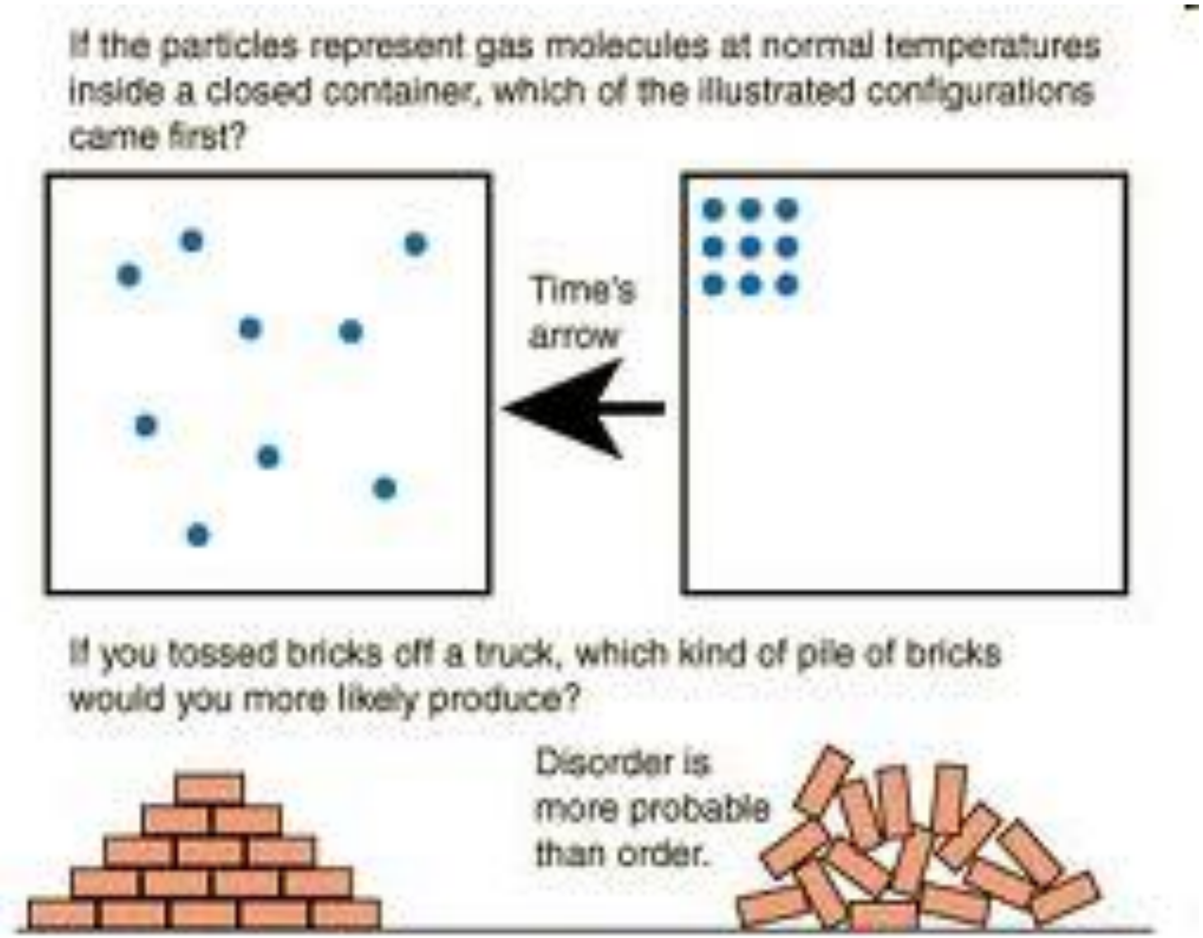
Arrangement	Microstates	Number of Microstates
IV		4
V		1

D A B C
B A D C
C A D B
A B D C
A B C D

Positional Entropy

- A gas expands into a vacuum because the expanded state has the highest positional probability of states available to the system.
- Therefore: $S_{solid} < S_{liquid} << S_{gas}$

Entropy: which are most probable?

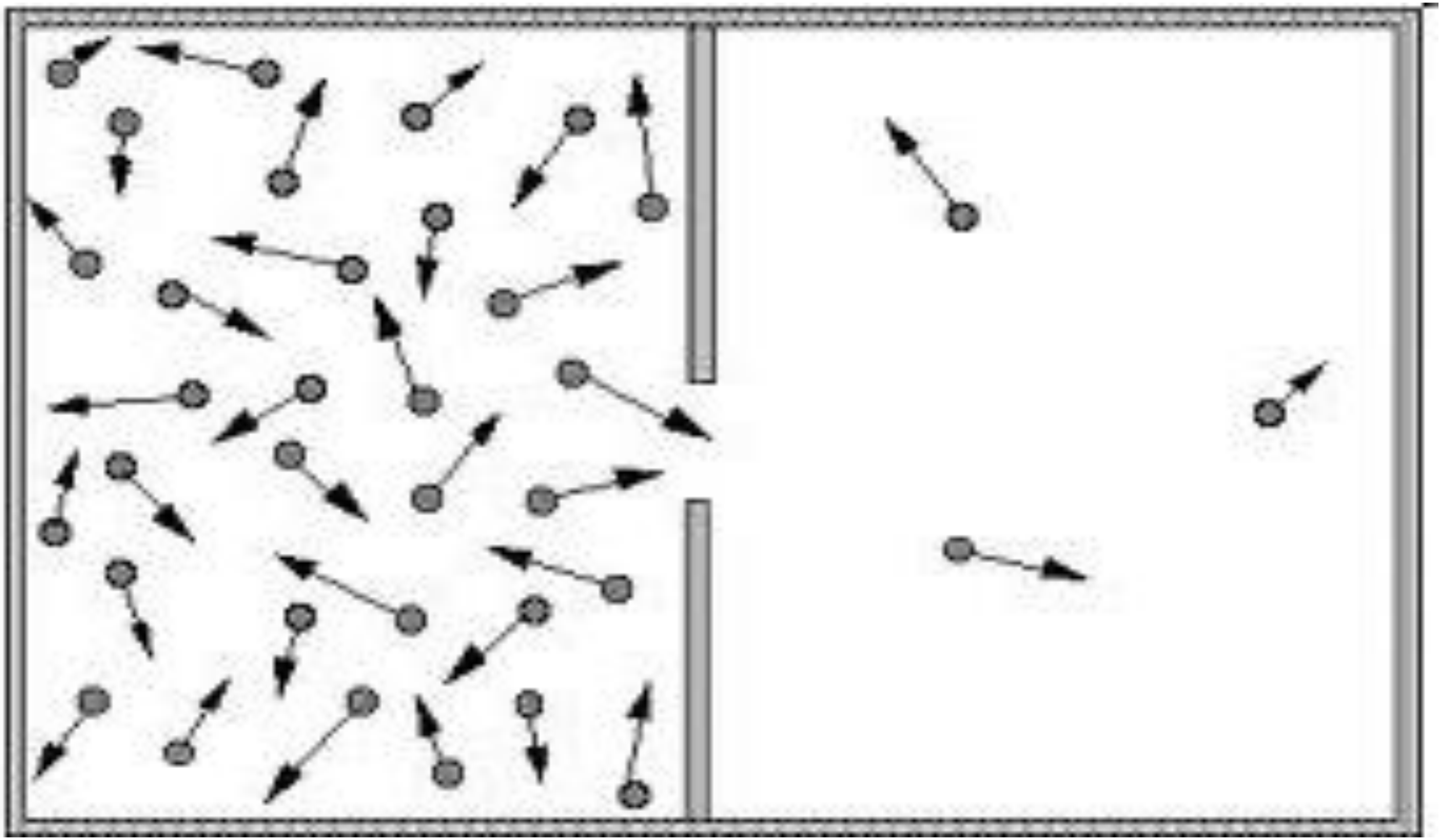


If the particles represent gas molecules at normal temperatures inside a closed container, which of the illustrated configurations came first?

If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?

Disorder is more probable than order.

Where do molecules have the higher entropy



Concept Check

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

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

Relative Entropy of Substances

- Entropy:
  - increases from solid to liquid to vapor/gas;
  - increases as temperature increases;
  - of gas increases as its volume increases at constant temperature;
  - increases when gases are mixed.
  - of elements increases down the group in the periodic table;
  - of compound increases as its structure becomes more complex.

Second Law of Thermodynamics

- In any spontaneous process there is always an increase in the entropy of the universe.
- The entropy of the universe is increasing.
- The total energy of the universe is constant, but the entropy is increasing.

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

Second Law of Thermodynamics

- *Energy* tends to flow from a *high energy concentration* to a *dispersed energy state*;
- Energy dispersion or diffusion is a *spontaneous* process.
- Dispersed or diffused energy is called ***entropy***
- According to *SLoT,* a process/reaction is *spontaneous* if the *entropy* of the *universe* (system + surrounding) *increases*.

Concept Check

Effect of Temperature on Spontaneity

For the process $A(l) \rightleftharpoons A(s)$, which direction involves an increase in energy randomness? Positional randomness? Explain your answer.

As temperature increases/decreases (answer for both), which takes precedence? Why?

At what temperature is there a balance between energy randomness and positional randomness?

Concept Check

Describe the following as spontaneous/non-spontaneous/cannot tell, and explain.

A reaction that is:

(a) Exothermic and becomes more positionally random

Spontaneous

(b) Exothermic and becomes less positionally random

Cannot tell

(c) Endothermic and becomes more positionally random

Cannot tell

(d) Endothermic and becomes less positionally random

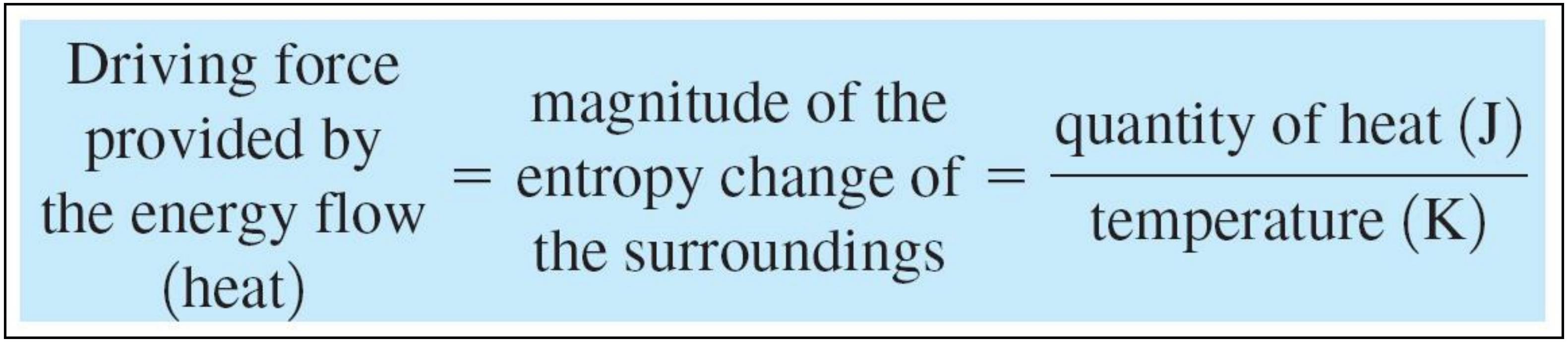
Not spontaneous

Explain how temperature affects your answers.

$\otimes S_{\text{surr}}$

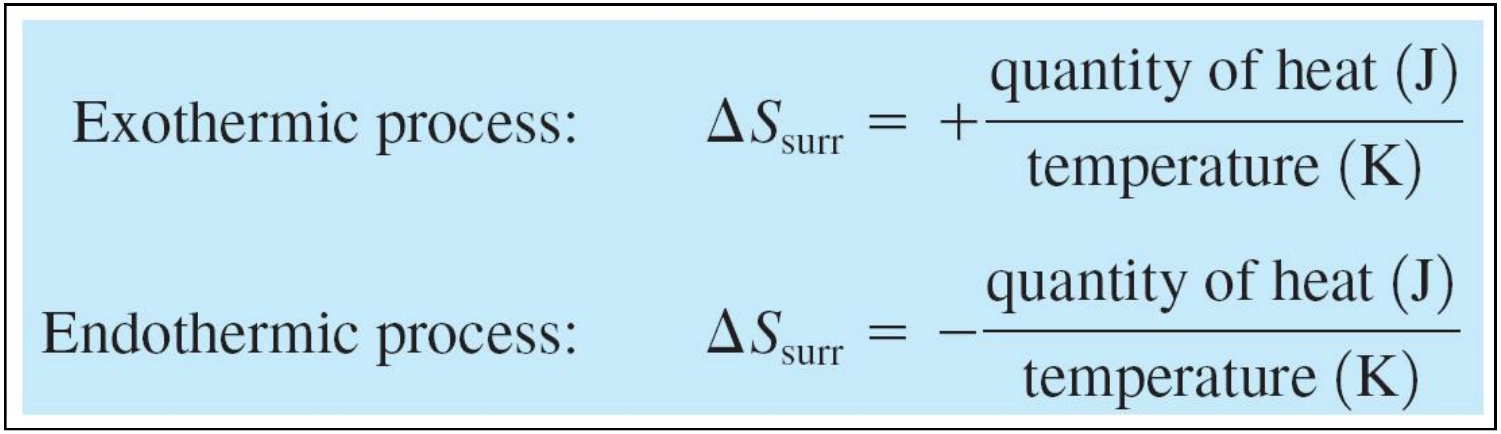
- The sign of $\otimes S_{\text{surr}}$ depends on the direction of the heat flow.
- The magnitude of $\otimes S_{\text{surr}}$ depends on the temperature.

$\otimes S_{\text{surr}}$



$$\text{Driving force provided by the energy flow (heat)} = \text{magnitude of the entropy change of the surroundings} = \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

$\otimes S_{\text{surr}}$



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

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

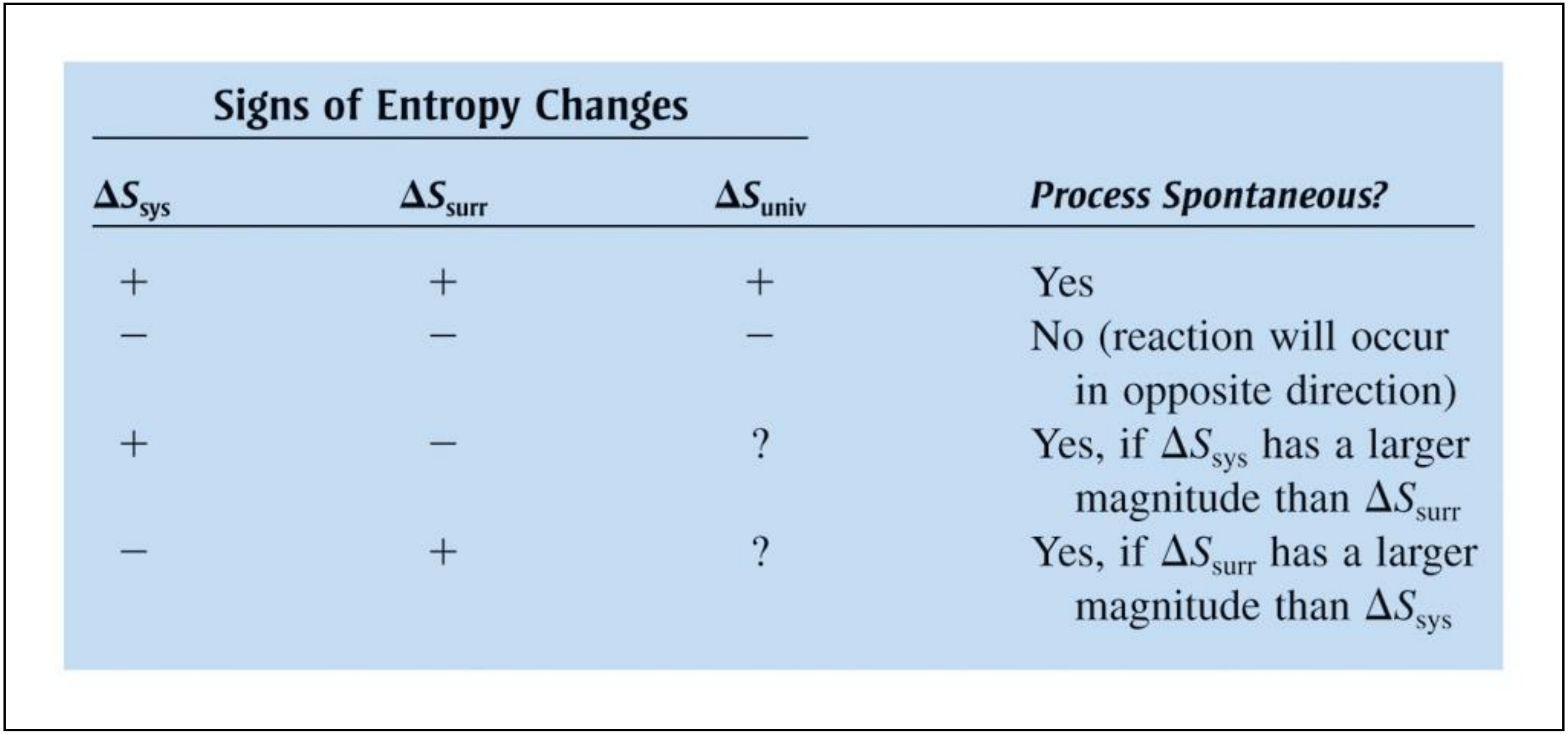
$\otimes S_{\text{surr}}$

Heat flow (constant *P*) = change in enthalpy

$= \otimes H$

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

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



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

Effect of Temperature on Δ*G* and Spontaneity

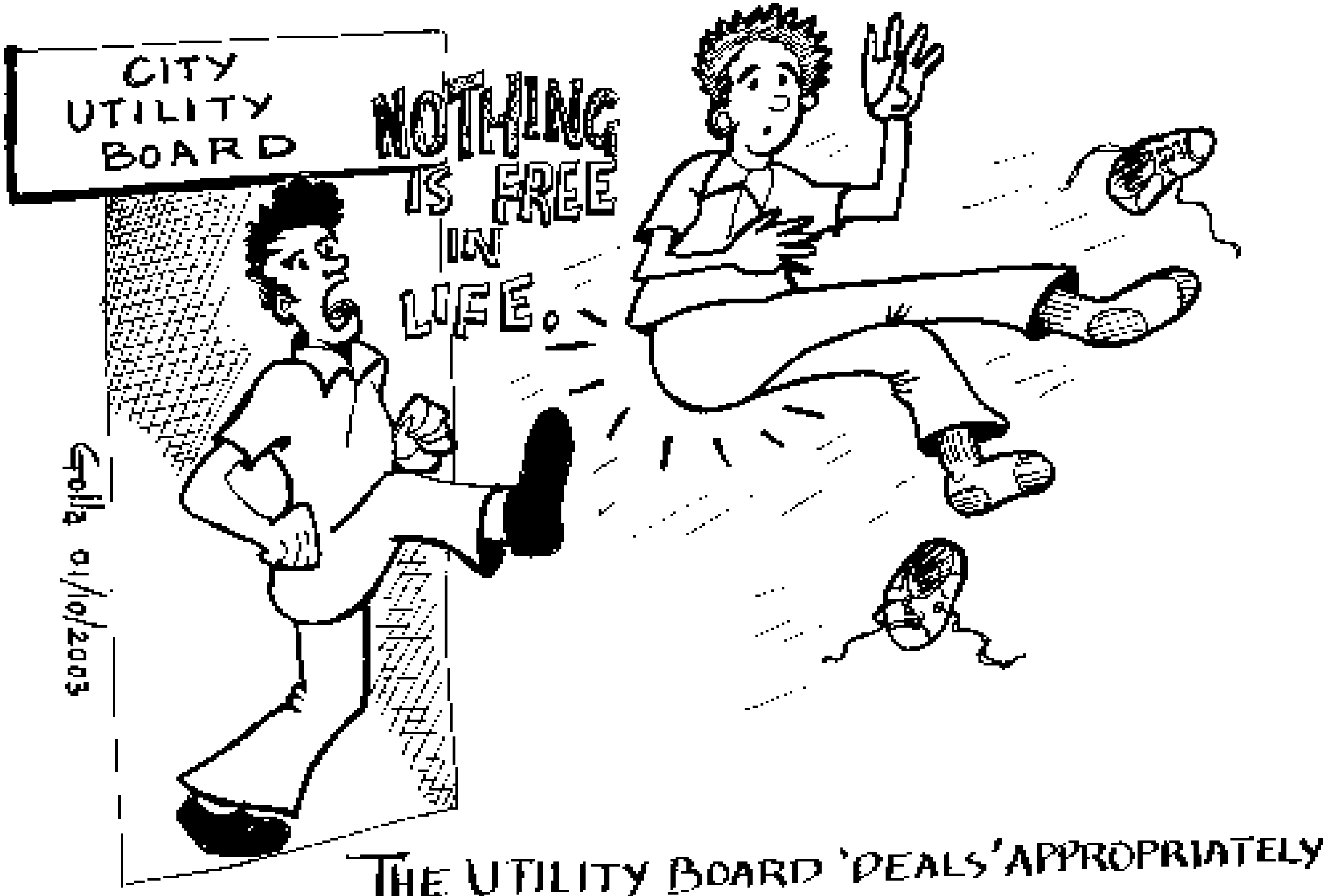
Δ*H*	Δ*S*	T	Δ*G*	Comments	Examples
-	+	high or low	-	spontaneous at all temperature	$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$
+	+	high	-	spontaneous at high temperature	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
-	-	low	-	spontaneous at low temperature	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
+	-	high or low	+	nonspontaneous at all temperature	$2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$

Free Energy (*G*)

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \text{ (at constant } T \text{ and } P\text{)}$$

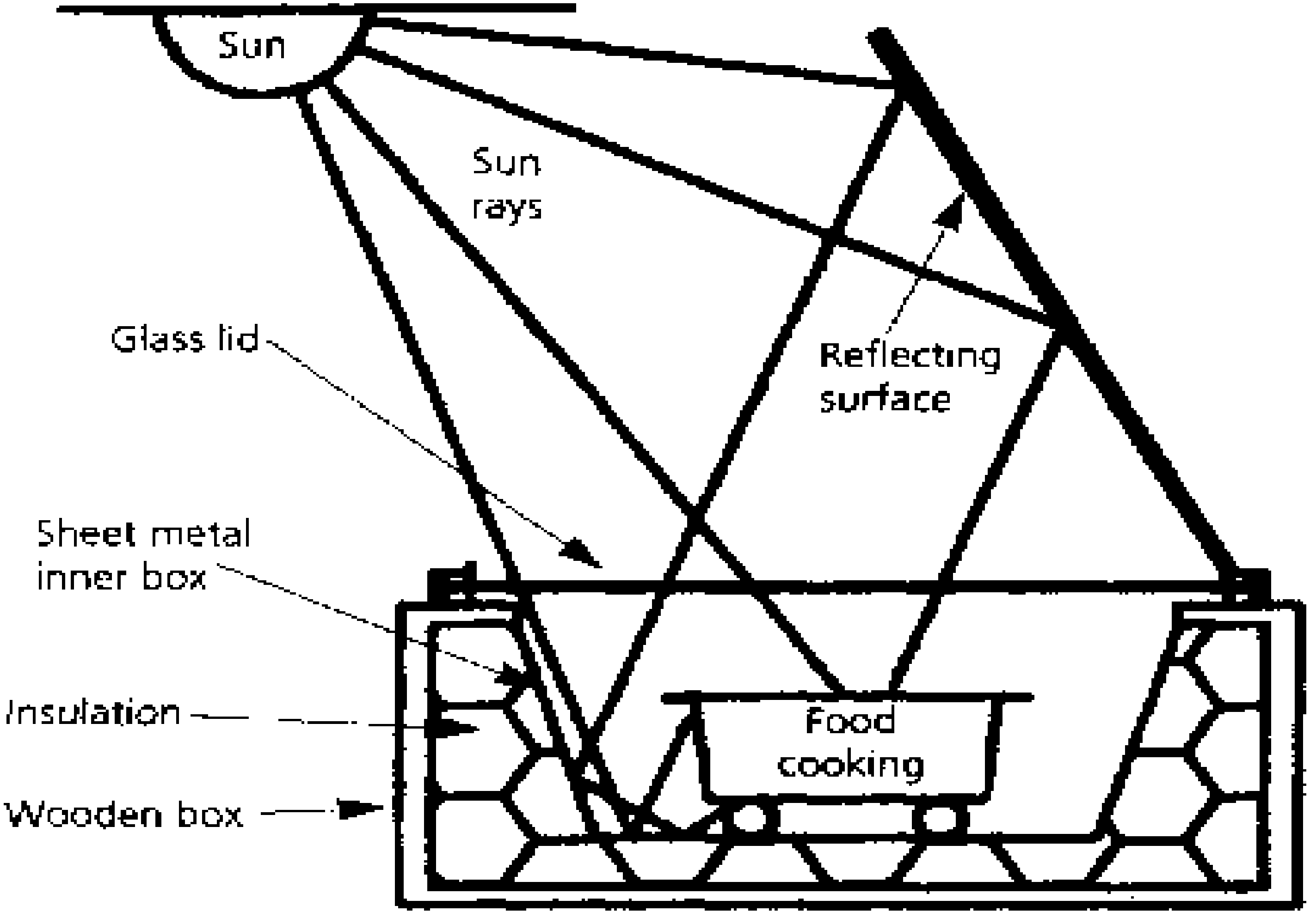
- A process (at constant *T* and *P*) is spontaneous in the direction in which the free energy decreases.
    - Negative ΔG means positive ΔS_{univ}.

What is Free Energy?


CITY UTILITY BOARD
NOTHING IS FREE IN LIFE.
Golla 01/10/2003

THE UTILITY BOARD 'DEALS' APPROPRIATELY WITH THE FREE ENERGY QUACK.

Free Energy?


Sun
Sun rays
Reflecting surface
Glass lid
Sheet metal inner box
Insulation
Wooden box
Food cooking

Free Energy (G)

- In Thermodynamic System:

  $\Delta G = \Delta H - T\Delta S$ (at constant T and P)

Gibb's Free Energy

- For spontaneous reactions,

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

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/\text{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/\text{T}$$

$$-\text{T}\Delta S_{\text{univ}} = \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - \text{T}\Delta S_{\text{sys}} < 0$$

ΔG_{sys} is called Gibb's *free energy*

- Another criteria for spontaneous process is $\Delta G_{\text{sys}} < 0$

Concept Check

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

w	–
q	+
ΔH	+
ΔS	+
ΔS_{surr}	–
ΔG	0

Explain your answers.

Exercise

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

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

$\Delta S = 132 \text{ J/K·mol}$

$\Delta S_{\text{surr}} = -132 \text{ J/K·mol}$

$\Delta G = 0 \text{ kJ/mol}$

Spontaneous Reactions

Effect of ΔH and ΔS on Spontaneity

ΔH	ΔS	Result
–	+	spontaneous at all temps
+	+	spontaneous at high temps
–	–	spontaneous at low temps
+	–	not spontaneous at any temp

Concept Check

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

Predict the signs of:

ΔH	ΔS_{surr}	ΔS	ΔS_{univ}
–	+	0	+

Explain.

Third Law of Thermodynamics

- The entropy of a perfect crystal at 0 K is zero.
- The entropy of a substance increases with temperature.

Standard Entropy Values ($S°$)

- Represent the increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm pressure.

$$\Delta S°_{\text{reaction}} = \Sigma n_{\text{p}} S°_{\text{products}} - \Sigma n_{\text{r}} S°_{\text{reactants}}$$

Exercise

Calculate $\Delta S°$ for the following reaction:

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$$

Given the following information:

	$S°$ (J/K·mol)
Na(s)	51
H_2O(l)	70
NaOH(aq)	50
H_2(g)	131

$\Delta S° = –11$ J/K

Standard Free Energy Change ($\Delta G°$)

- The change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.

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

$$\Delta G°_{\text{reaction}} = \Sigma n_{\text{p}} G°_{\text{products}} - \Sigma n_{\text{r}} G°_{\text{reactants}}$$

Concept Check

Consider the following system at equilibrium at 25°C.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

$$\Delta G^\circ = -92.50 \text{ kJ}$$

What will happen to the ratio of partial pressure of PCl_5 to partial pressure of PCl_3 if the temperature is raised? Explain.

The ratio will decrease.

Free Energy and Pressure

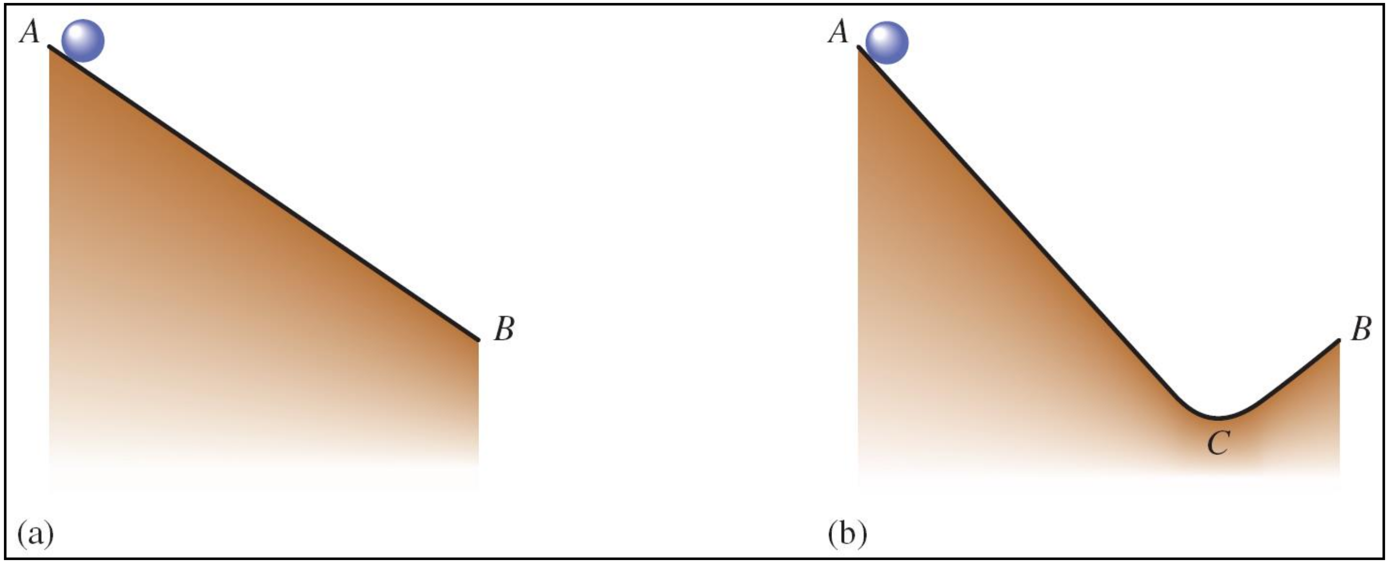
$$G = G^\circ + RT \ln(P)$$

or

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

The Meaning of Δ*G* for a Chemical Reaction

- A system can achieve the lowest possible free energy by going to equilibrium, not by going to completion.



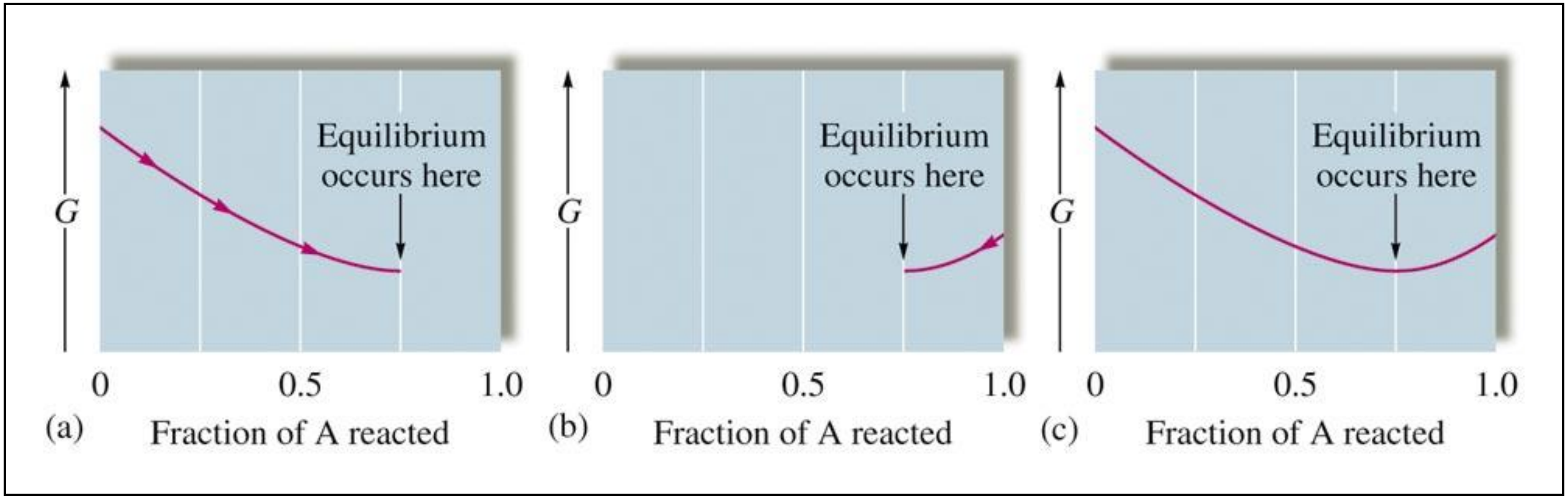
Free Energy and Equilibrium

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

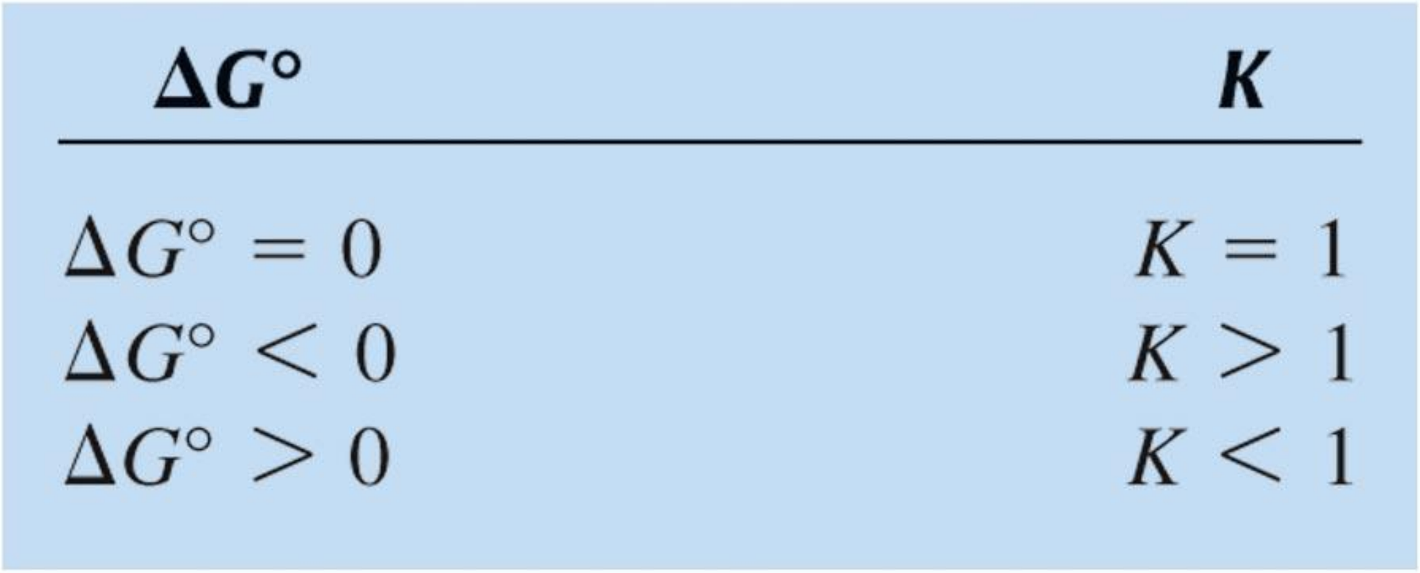
$$\Delta G = 0 = \Delta G^\circ + RT\ln(K)$$

$$\Delta G^\circ = -RT\ln(K)$$

Change in Free Energy to Reach Equilibrium



Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction



ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Free Energy and Work

- Maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy.

$$w_{\mathrm{max}} = \Delta G$$

Free Energy and Work

- Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway. Any real pathway wastes energy.
- All real processes are irreversible.
- First law: You can’t win, you can only break even.
- Second law: You can’t break even.

Third Law of Thermodynamics

- *The entropy of a perfect crystalline substance is zero at absolute zero temperature (0.0 K)*

- Is absolute zero temperature achievable?

Standard Entropy, S^o

- The entropy of a substance in its most stable state at 1 atm and 25°C.
- The entropy of an ionic species in 1 *M* solution at 25°C.

Entropy and Second Law of Thermodynamics

- The *second law of thermodynamics* states that all spontaneous processes are accompanied by increase in the entropy of the *universe*.
  - Universe = System + Surrounding;
  - System: the process/reaction whose thermodynamic change is being studied;
  - Surrounding: the part of the universe that interacts with the system.

Conditions for Spontaneous Process

- Entropy change for a process:

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0,$ ➔ process is spontaneous

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0,$ ➔ process is at equilibrium

- If $\Delta S_{sys} < 0$, $\Delta S_{surr} > 0$, and $|\Delta S_{surr}| > |\Delta S_{sys}|$
- If $\Delta S_{surr} < 0$, $\Delta S_{sys} > 0$, and $|\Delta S_{sys}| > |\Delta S_{surr}|$

Thermodynamic Free Energy

- It is the maximum amount of chemical energy derived from a spontaneous reaction that can be utilized to do work or to drive a *nonspontaneous* process.

- It is the minimum amount of energy that must be supplied to make a nonspontaneous reaction occur.

Entropy Change in Chemical Reactions

- At constant temperature and pressure,

$$\Delta S^{o}_{\text{rxn}} = \Sigma n_{\text{p}} S^{o}_{\text{products}} - \Sigma n_{\text{r}} S^{o}_{\text{reactants}}$$

- In general, $\Delta S^{o}_{\text{rxn}} > 0$ if $\Sigma n_{\text{p}} > \Sigma n_{\text{r}}$

- Example-1:
- $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$, $(\Sigma n_p > \Sigma n_r)$

  $\Delta S^{o}_{\text{rxn}} = \{(3 \text{ x } S^{o}_{CO_2}) + (4 \text{ x } S^{o}_{H_2O})\} - \{(S^{o}_{C_3H_8}) + (5 \text{ x } S^{o}_{O_2})\}$
- $= \{(3 \text{ x } 214) + (4 \text{ x } 189)\}\text{J/K} - \{270 + (5 \text{ x } 205)\}\text{J/K}$
- $= (642 + 756) \text{ J/K} - (270 + 1025) \text{ J/K}$

  $= 103 \text{ J/K}$

Entropy Change in Chemical Reactions

$\Delta S^{o}_{rxn} < 0$ if $\Sigma n_{p} < \Sigma n_{r}$

- Example-2:
- $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$, $(\Sigma n_{p} < \Sigma n_{r})$

  $\Delta S^{o}_{rxn} = (S^{o}_{CH_3OH}) - \{(S^{o}_{CO}) + (2 \text{ x } S^{o}_{H_2})\}$
- = 240 J/K – {198 J/K + (2 x 131 J/K)
- = 240 J/K – 460 J/K = -220 J/K

Effect of Temperature on ΔG^o

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

- Example-1:
- For the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$,

  $\Delta H^o = -92$ kJ and $\Delta S^o = -199$ J/K $= -0.199$ kJ/K

- At 25°C, $T\Delta S^o = 298 \text{ K} \times (-0.199 \text{ J/K}) = -59.3$ kJ
- $\Delta G^o = \Delta H^o - T\Delta S^o = -92 \text{ kJ} – (-59.3 \text{ kJ}) = -33$ kJ;
- ➔ reaction is *spontaneous* at 25°C

- At 250°C, $T\Delta S^o = 523 \text{ K} \times (-0.199 \text{ J/K}) = -104$ kJ;
- $\Delta G^o = \Delta H^o - T\Delta S^o = -92 \text{ kJ} – (-104 \text{ kJ}) = 12$ kJ;
- ➔ reaction is *nonspontaneous* at 250°C

Effect of Temperature on ΔG^o

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

- Example-2:
- For the reaction: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$,
  $\Delta H^o = 206$ kJ and $\Delta S^o = 216$ J/K = 0.216 kJ/K

- At 25°C, $T\Delta S^o = 298$ K x (0.216 J/K) = 64.4 kJ
- $\Delta G^o = \Delta H^o - T\Delta S^o = 206$ kJ – 64.4 kJ = 142 kJ;
- ➔ reaction is *nonspontaneous* at 25°C.

- At 1200 K, $T\Delta S^o = 1200$ K x (0.216 J/K) = 259 kJ;
- $\Delta G^o = \Delta H^o - T\Delta S^o = 206$ kJ – 259 kJ) = -53 kJ;
- ➔ reaction is spontaneous at 1200 K

ΔG under Nonstandard Conditions

- Free energy change also depends on concentrations and partial pressures;
- Under *nonstandard conditions* (P_i not 1 atm),

$$\Delta G = \Delta G^o + RT\,lnQ_p,$$

Consider the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$,

$$Q_p = \frac{(P_{NH3})^2}{(P_{N2})(P_{H2})^3}$$

Under *standard condition*, $P_{N_2} = P_{H_2} = P_{NH_3} = 1$ atm, $Q_p = 1$;

$lnQ_p = 0$, and $\Delta G = \Delta G^o$

ΔG of reaction under *nonstandard condition*

Consider the following reaction at 250°C:

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

where, P_{N_2} = 5.0 atm, P_{H_2} = 15 atm, and P_{NH_3} = 5.0 atm

$$Q_p = 5^2/(5 \text{ x } 15^3) = 1.5 \text{ x } 10^{-3}$$
$$lnQ_p = ln(1.5 \text{ x } 10^{-3}) = -6.5$$

Under this condition, $\Delta G = \Delta G^o + RTlnQ_p$;

(For this reaction at 250°C, calculated ΔG^o = 12 kJ)

$$\therefore \ \Delta G = 12 \text{ kJ} + (0.008314 \text{ kJ/T x } 523 \text{ K x } (-6.5))$$
$$= 12 \text{ kJ} - 28 \text{ kJ} = -16 \text{ kJ}$$ ➔ spontaneous reaction

Transition Temperature

- This is a temperature at which a reaction changes from being *spontaneous* to being *nonspontaneous*, and *vice versa*, when Q_p or Q_c equals 1 (standard condition)

- At transition temperature, T_r,

$$\Delta G^o = \Delta H^o - T_r\Delta S^o = 0; \;\rightarrow\; T_r = \Delta H^o/\Delta S^o$$

For reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$,

$$T_r = -92\text{ kJ}/(-0.199\text{ kJ/K}) = 460\text{ K} = 190^oC$$

Under standard pressure (1 atm), this reaction is spontaneous below 190°C, but becomes *nonspontaneous* above this temperqature.

Transition Temperature

- For reaction: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$,

  $\Delta H^o = 206$ kJ and $\Delta S^o = 216$ J/K = 0.216 kJ/K

  $\Delta G^o = \Delta H^o + T_r\Delta S^o = 0$,

  $T_r = 206$ kJ/(0.216 kJ/K) = 954 K = 681°C

  Under standard pressure (1 atm), this reaction is not spontaneous below 681°C, but becomes spontaneous above this temperature.

  Reactions with both ΔH^o and $\Delta S^o < 0$ favor low temperature;

  Those with both ΔH^o and $\Delta S^o > 0$ favor high temperature.

Free Energy and Equilibrium Constant

- For spontaneous reactions, ΔG decreases (becomes less negative) as the reaction proceeds towards equilibrium;
- At equilibrium, $\Delta G = 0$;
- $\Delta G = \Delta G^{o} + \mathrm{RT}\,lnK = 0$
- $\Delta G^{o} = -\mathrm{RT}\,lnK$
- $lnK = -\Delta G^{o}/\mathrm{RT}$ (ΔG^{o} calculated at temperature T)
- Equilibrium constant, $K = e^{-(\Delta G^{o}/\mathrm{RT})}$

ΔGo < 0, $K > 1$; reaction favors products formation

ΔGo > 0, $K < 1$; reaction favors reactants formation

ΔGo = 0, $K = 1$; reaction favors neither reactants nor products

Calculating K from ΔG^o

- Consider the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$,

- At 25°C, $\Delta G^o = -33$ kJ
- $lnK = -(-33 \times 10^3 \text{ J}/(298 \text{ K} \times 8.314 \text{ J/K.mol})) = 13$
- $K = e^{13} = 4.4 \times 10^5$ (reaction goes to completion)

- At 250°C, $\Delta G^o = 12$ kJ;
- $lnK = -(12 \times 10^3 \text{ J}/(523 \text{ K} \times 8.314 \text{ J/K.mol})) = -2.8$
- $K = e^{-2.8} = 0.061$ (very little product is formed)

Coupling Reactions

- A nonspontaneous reaction can be coupled to a spontaneous one to make it happen.

Example:

- $Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + 3/2\ O_{2(g)}$; $\Delta G^o = 740$ kJ (eq-1)
- $CO_{(g)} + ½\ O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta G^o = -283$ kJ
- $3CO_{(g)} + 3/2\ O_{2(g)} \rightarrow 3CO_{2(g)}$; $\Delta G^o = -849$ kJ (eq-2)

Combining eq-1 and eq-2,

- $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$; $\Delta G^o = -109$ kJ

Coupling Reactions in Biological System

- The formation of ATP from ADP and $H_2PO_4^-$ is nonspontaneous, but it can be coupled to the hydrolysis of creatine-phosphate that has a negative ΔG^o.

- ADP + $H_2PO_4^-$ → ATP + H_2O; $\Delta G^o = +30$ kJ
- Creatine-phosphate → creatine + phosphate; $\Delta G^o = -43$ kJ

Combining the two equations yields a spontaneous overall reaction:

- Creatine-phosphate + ADP → Creatine + ATP; $\Delta G^o = -13$ kJ