

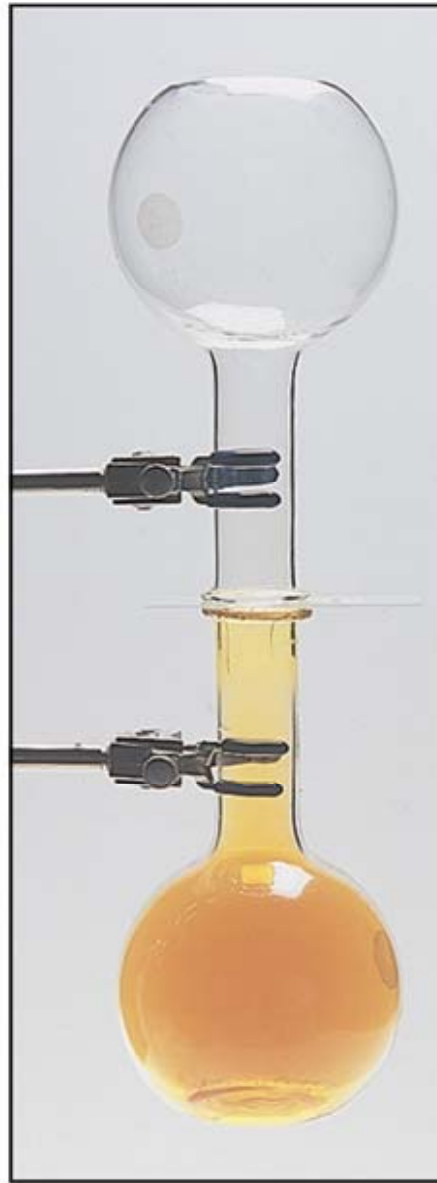
# Chapter 18

## **Thermodynamics: Directionality of Chemical Reactions**

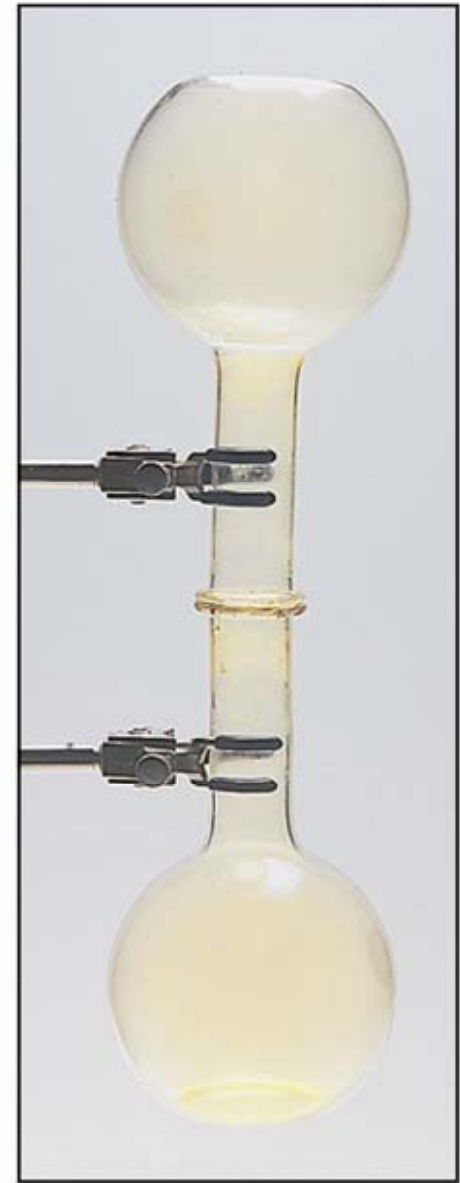
# Dispersal of Energy

- the probability is higher when energy is dispersed over a larger number of particles
- matter tends to disperse unless it is restricted

# Expansion of a Gas

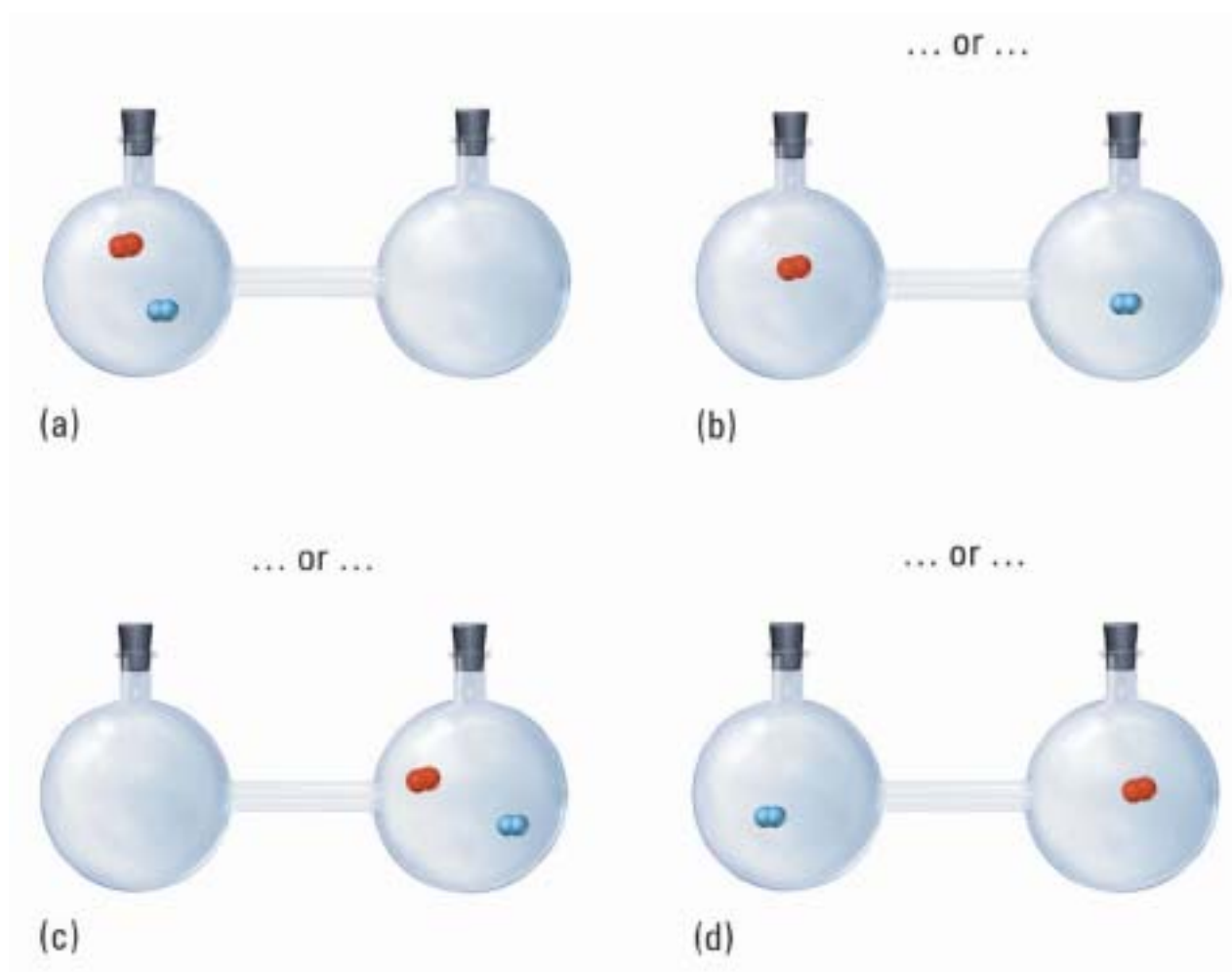


(a)



(b)

# Gas Expansion and Probability



# Entropy

- Quantity specifying the amount of disorder or randomness in a system bearing energy or information
- Boltzmann Equation

$$S = k \log W$$

where  $W \Rightarrow$  thermodynamic probability

- effected by degree of motion
- complexity of shape
- Mixing with other species
- $\Delta S = S_{\text{final}} - S_{\text{initial}}$

# Standard Molar Entropy Values

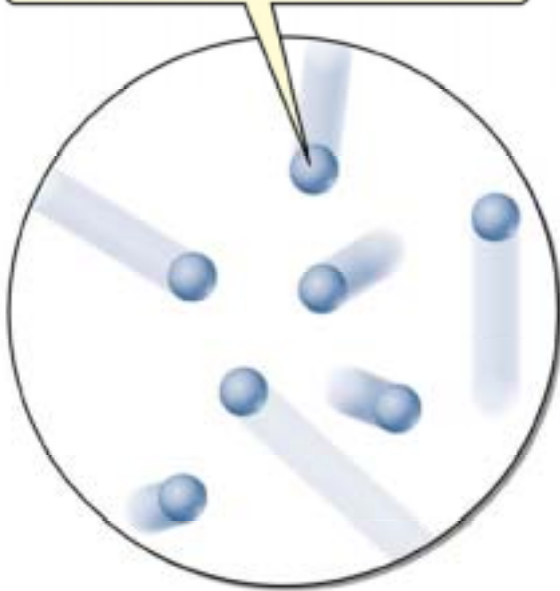
**TABLE 18.1** Some Standard Molar Entropy Values at 298.15 K\*

Compound or element	Entropy, $S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	Compound or element	Entropy, $S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	Compound or element	Entropy, $S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
C(graphite)	5.740	Br <sub>2</sub> (ℓ)	152.231	Ca(s)	41.42
C(g)	158.096	I <sub>2</sub> (s)	116.135	NaF(s)	51.5
CH <sub>4</sub> (g)	186.264	Ar(g)	154.7	MgO(s)	26.94
CH <sub>3</sub> CH <sub>3</sub> (g)	229.60	H <sub>2</sub> (g)	130.684	NaCl(s)	72.13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> (g)	269.9	N <sub>2</sub> (g)	191.61	KOH(s)	78.9
CH <sub>3</sub> OH(ℓ)	126.8	O <sub>2</sub> (g)	205.138	MgCO <sub>3</sub> (s)	65.7
CO(g)	197.674	NH <sub>3</sub> (g)	192.45	NH <sub>4</sub> NO <sub>3</sub> (s)	151.08
CO <sub>2</sub> (g)	213.74	HCl(g)	186.908	NaCl(aq)	115.5
F <sub>2</sub> (g)	202.78	H <sub>2</sub> O(g)	188.825	NH <sub>4</sub> NO <sub>3</sub> (aq)	259.8
Cl <sub>2</sub> (g)	223.066	H <sub>2</sub> O(ℓ)	69.91	KOH(aq)	91.6

\* Data from Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R. The NBS Tables of Chemical Thermodynamic Properties, *Journal of Physical and Chemical Reference Data*, Vol. 11, Suppl. 2, 1982.

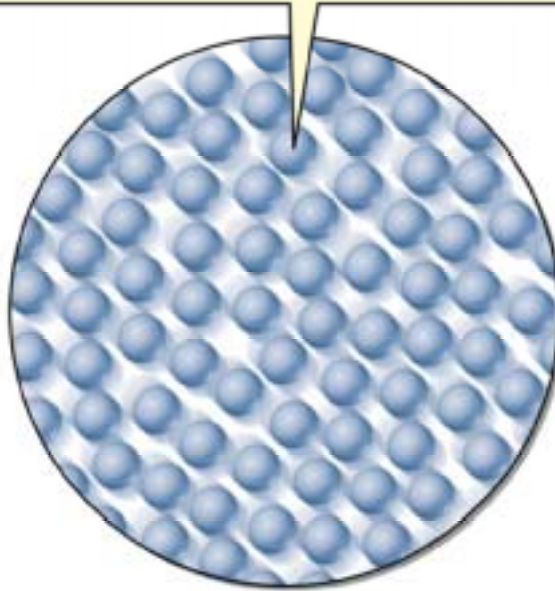
# Entropies of Solid, Liquid and Gas Phases

The particles in a gas move in random directions at random speeds.



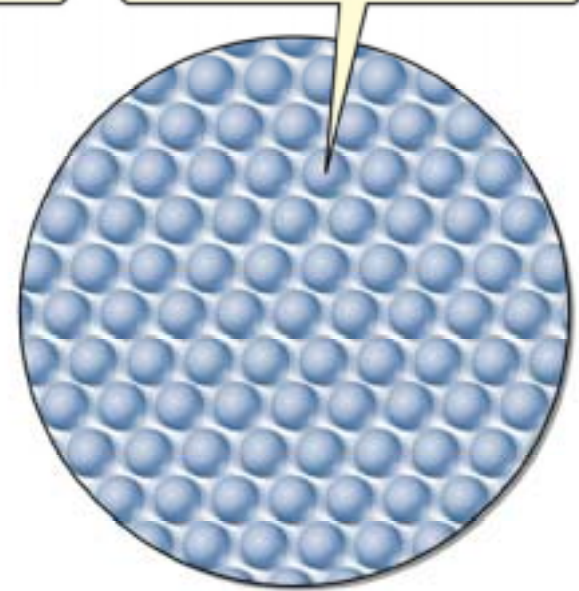
Gas

Particles in a liquid are more concentrated than in a gas, but move randomly and have no fixed positions.



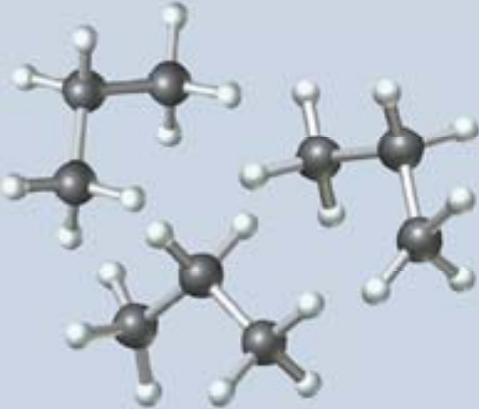
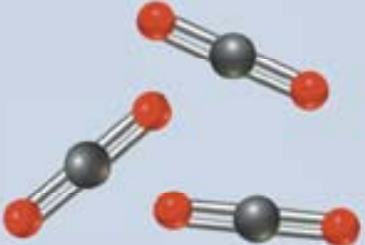

Liquid

Particles in a solid are constrained to vibrate about specific positions.



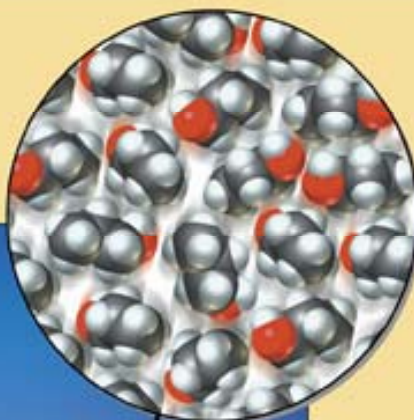
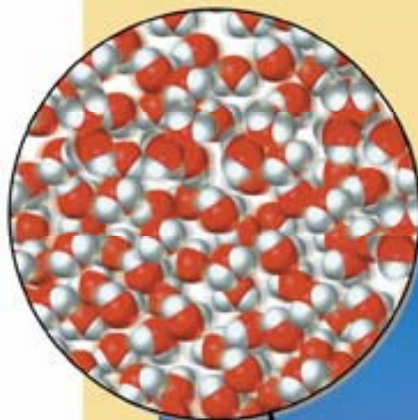
Solid

# Entropy and Molecular Structure

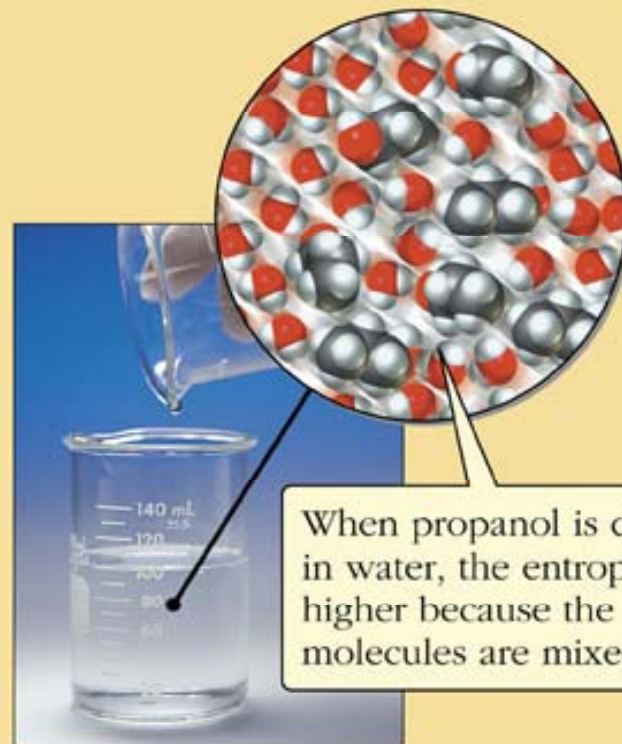
Name	Propane	Carbon dioxide	Argon
Molecular model			
Entropy ( $\text{J K}^{-1} \text{mol}^{-1}$ )	269.9	213.74	154.7
Molar mass (g/mol)	44.1	44.0	39.9



# Entropy and Dissolving

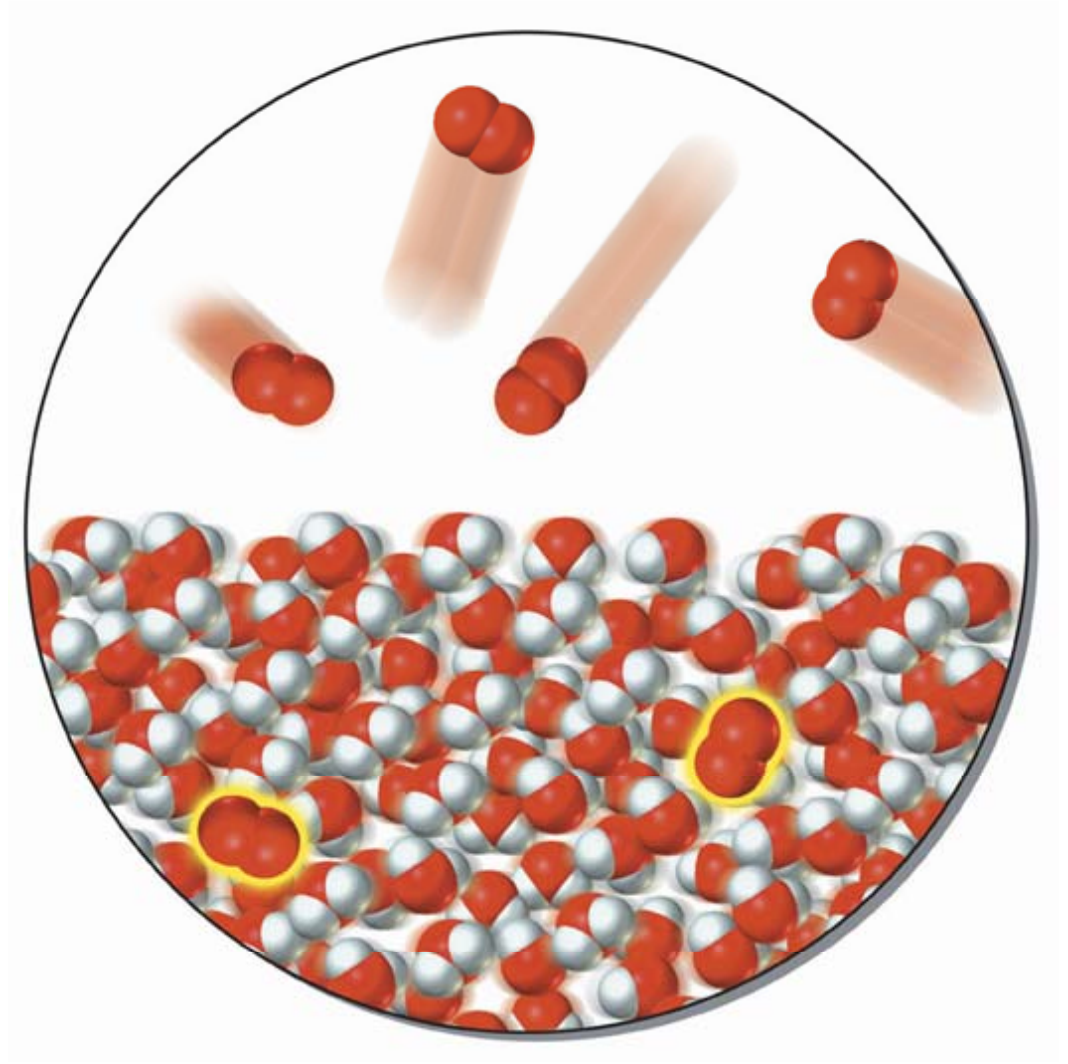


(a)



(b)

# Entropy of a Solution of a Gas



# Qualitative Guidelines for Entropy

- entropies of gases higher than liquids higher than solids
- entropies are higher for more complex structures than simpler structures
- entropies of ionic solids are inversely related to the strength of ionic forces
- entropy increases when making solutions of solids or liquids in a liquid solvent
- entropy decrease when making solutions of gases in a liquid

# Calculating Entropy Changes

$$\Delta S^{\circ} = \Sigma\{(\text{\#moles of product}) \times S^{\circ}_{\text{product}}\} \\ - \Sigma\{(\text{\#moles of reactant}) \times S^{\circ}_{\text{reactant}}\}$$

# Spontaneity

- How can water boil and freeze spontaneously?
- diamond and oxygen gas react to produce carbon dioxide, carbon dioxide can not spontaneously convert back into a diamond and oxygen gas
- gases spontaneously expand into a vacuum
- hot objects spontaneously cool

Enthalpy change can not predict spontaneity!

Need another thermodynamic property.

# Chemical Thermodynamics

- Spontaneous reaction – reaction which proceed without external assistance once started
- Chemical thermodynamics helps predict which reactions are spontaneous

# Entropy $\Rightarrow S$

- system - that part of the universe under investigation
- surroundings - rest of the universe
- universe - combination of system and surroundings

# Second Law of Thermodynamics

- in the universe the ENTROPY cannot decrease for any spontaneous process
- the entropy of the universe strives for a maximum
- in any spontaneous process, the entropy of the *universe* increases

$$\Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0$$



# Third Law of Thermodynamics

- all pure, perfectly crystalline substances at absolute zero have zero entropy

# Entropy Changes in the Surroundings

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$$

$$\Delta H_{\text{system}} = -T\Delta S_{\text{surroundings}}$$

at constant T & P

# Gibbs Free Energy and Work

- the difference between the enthalpy of a system and the product of its absolute temperature and entropy
- predictor of spontaneity

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

$$G = H - TS$$

$$\Delta G = \Delta H_{\text{system}} - T \Delta S_{\text{system}}$$

# Gibbs Free Energy and Equilibrium

$\Delta G$	Reaction
Negative	Spontaneous
Positive	Non-Spontaneous
Zero	Equilibrium

# Calculating Gibbs Free Energy Changes

$$\Delta G^{\circ} = \Sigma\{(\text{\#moles of product}) \times \Delta G_{\text{f product}}^{\circ}\} \\ - \Sigma\{(\text{\#moles of reactant}) \times \Delta G_{\text{f reactant}}^{\circ}\}$$

# The Influence of Temperature on Free Energy

$\Delta G$ ,  $\Delta H$ , &  $\Delta S$

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

$\Delta H$

negative

$\Delta S$

positive

$\Delta G$

negative

spontaneous at all temperatures

# The Influence of Temperature on Free Energy

$\Delta G$ ,  $\Delta H$ , &  $\Delta S$

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

$\Delta H$

$\Delta S$

$\Delta G$

positive

negative

positive

non-spontaneous at all temperatures

# The Influence of Temperature on Free Energy

$\Delta G$ ,  $\Delta H$ , &  $\Delta S$

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

$\Delta H$

$\Delta S$

$\Delta G$

negative

negative

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spontaneous at low temperatures,  
nonspontaneous at high temperatures



# The Influence of Temperature on Free Energy

$\Delta G$ ,  $\Delta H$ , &  $\Delta S$

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

$\Delta H$

$\Delta S$

$\Delta G$

positive

positive

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spontaneous at high temperatures,  
nonspontaneous at low temperatures

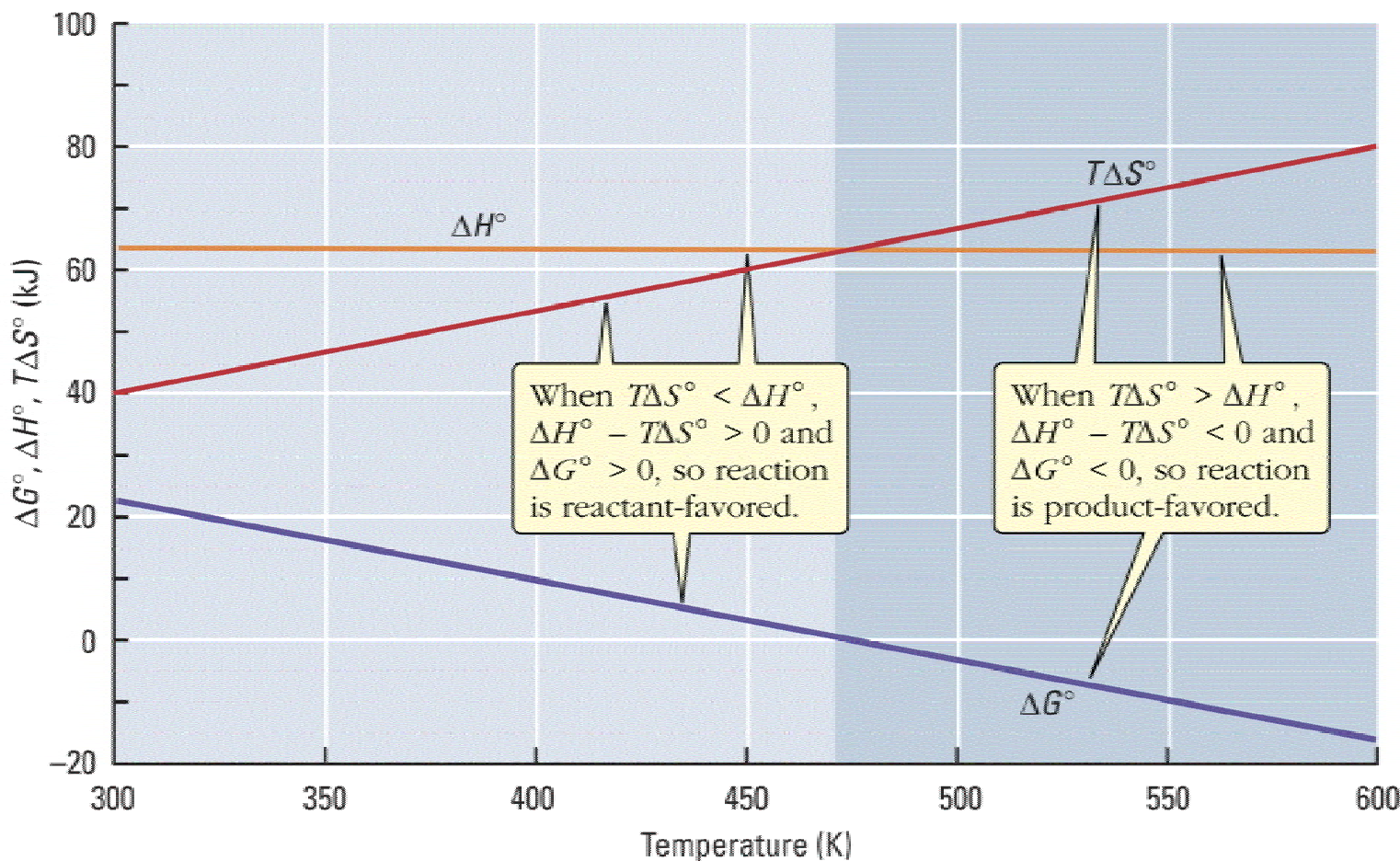
# Predicting Whether a Reaction is Product Favored

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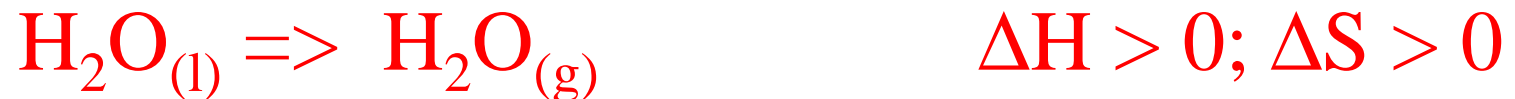
<b>Sign of <math>\Delta H_{\text{system}}</math></b>	<b>Sign of <math>\Delta S_{\text{system}}</math></b>	<b>Product-favored?</b>
Negative (exothermic)	Positive	Yes
Negative (exothermic)	Negative	Yes at low $T$ ; no at high $T$
Positive (endothermic)	Positive	No at low $T$ ; yes at high $T$
Positive (endothermic)	Negative	No

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# Effect of Temperature on Reaction Spontaneity

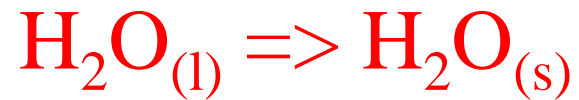


# Phase Transitions

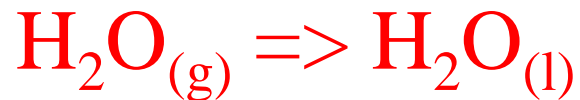


spontaneous at high temperatures

# Phase Transitions



$$\Delta H < 0; \Delta S < 0$$



$$\Delta H < 0; \Delta S < 0$$

spontaneous at low temperatures

# Phase Transitions

## Heat of Fusion

- energy associated with phase transition  
solid-to-liquid or liquid-to-solid

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

$$0 = \Delta H_{\text{fusion}} - T \Delta S_{\text{fusion}}$$

$$\Delta H_{\text{fusion}} = T \Delta S_{\text{fusion}}$$

# Phase Transitions

## Heat of Vaporization

- energy associated with phase transition gas-to-liquid or liquid-to-gas

$$\Delta H_{\text{vaporization}} = T \Delta S_{\text{vaporization}}$$

# Concentrations, Free Energy, and the Equilibrium Constant

## Concentration and Free Energy

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

## Equilibrium Constant and Free Energy

$$\Delta G = 0$$

$$0 = \Delta G^\circ + RT \ln K_{\text{eq}}$$

$$\Delta G^\circ = - RT \ln K_{\text{eq}}$$



# Concentrations, Free Energy, and the Equilibrium Constant

## Temperature and Equilibrium Constant

$$\ln K_{\text{eq}} = \Delta S^\circ/R - \Delta H^\circ/RT$$

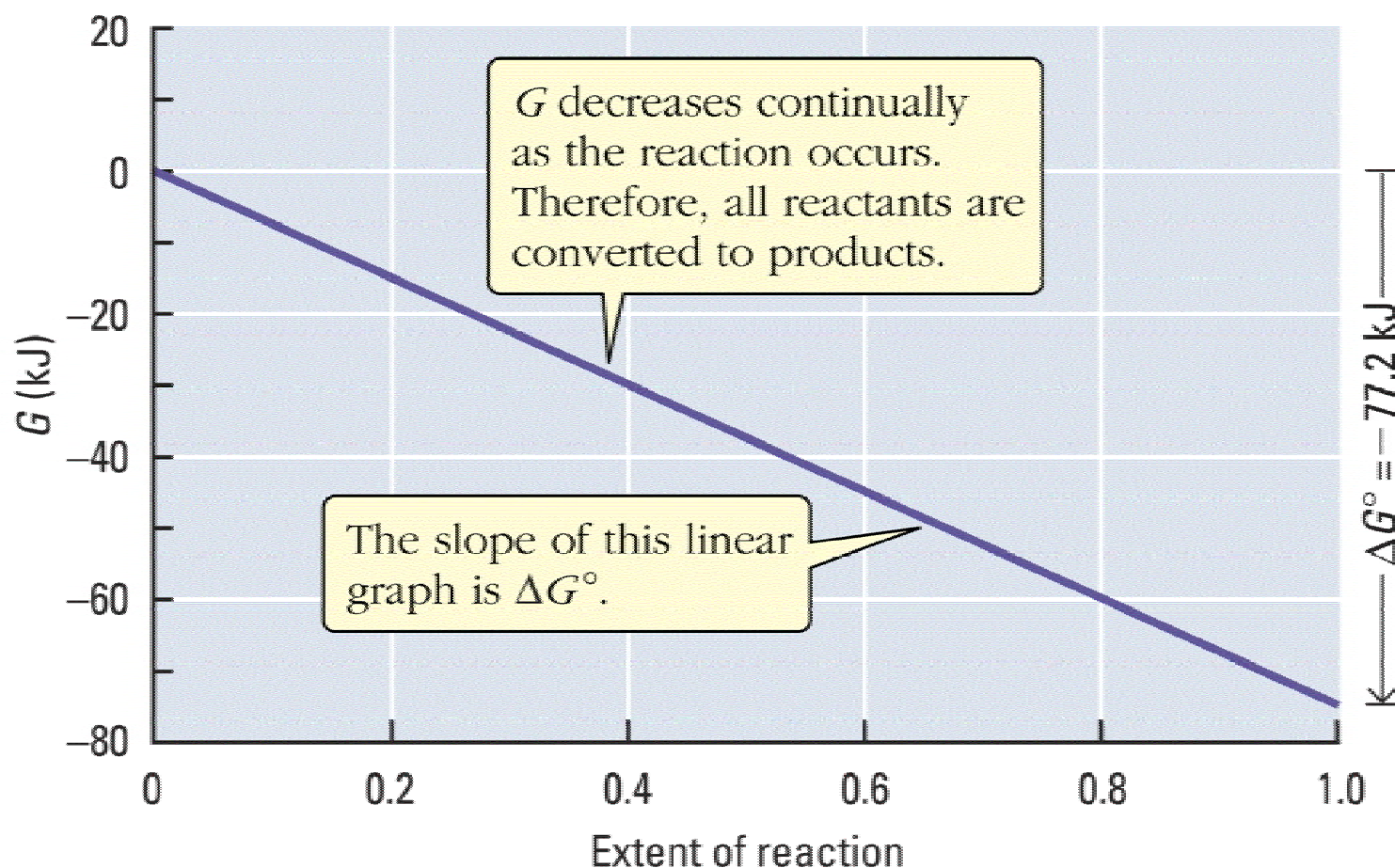
## The Influence of Temperature on Vapor Pressure



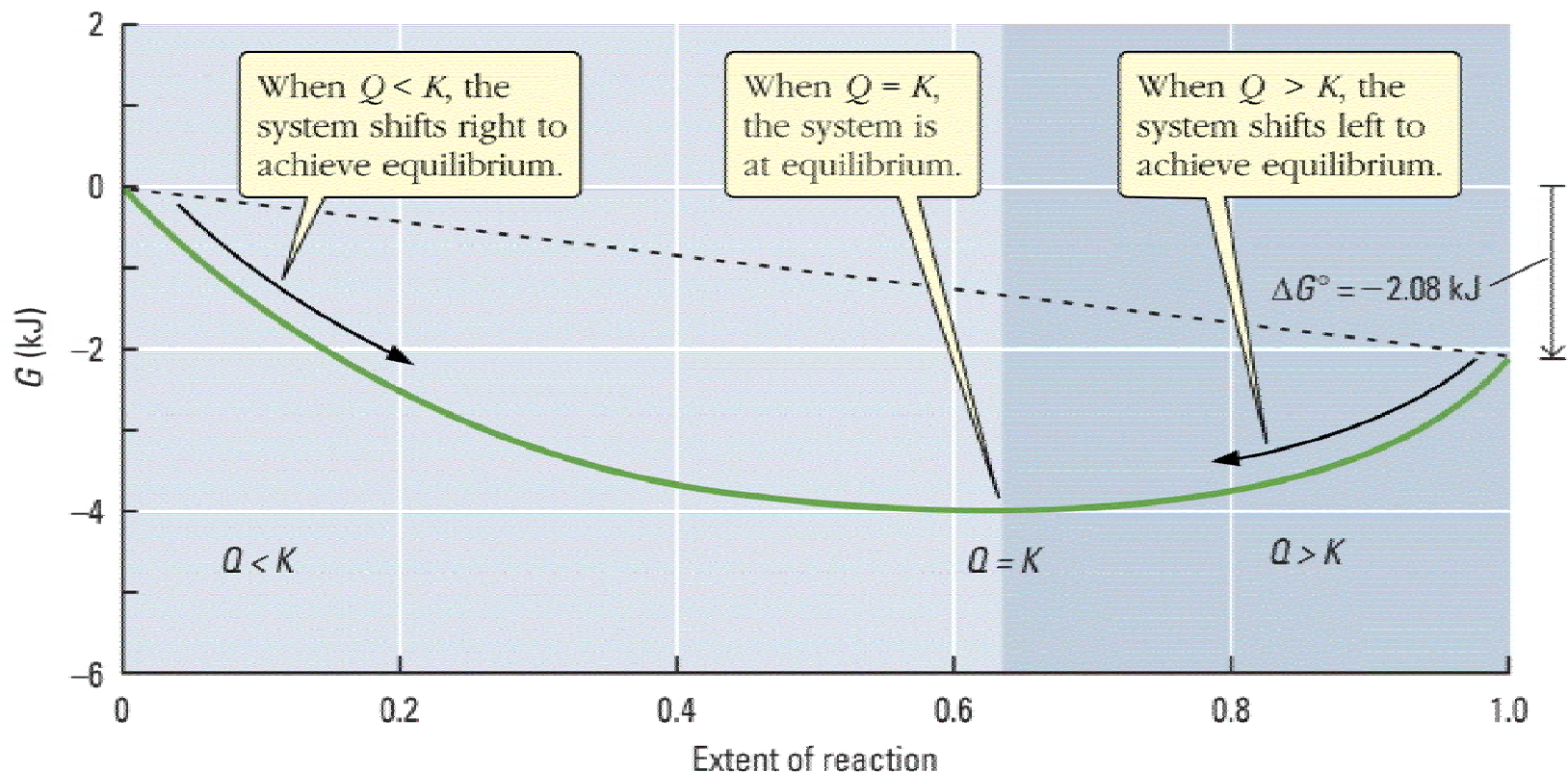
$$K_{\text{eq}} = p_{\text{water vapor}}$$

$$p_{\text{water vapor}} = K_{\text{eq}} = e^{-\Delta G^\circ/RT}$$

# $\Delta G$ as a Function of the Extent of the Reaction



# $\Delta G$ as a Function of the Extent of the Reaction when there is Mixing



# Maximum Work

$$\Delta G = w_{\text{system}} = - w_{\text{max}}$$

(work done on the surroundings)

# Photosynthesis

