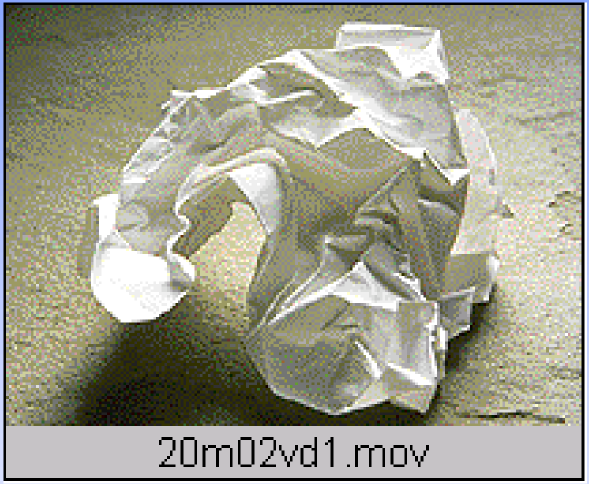
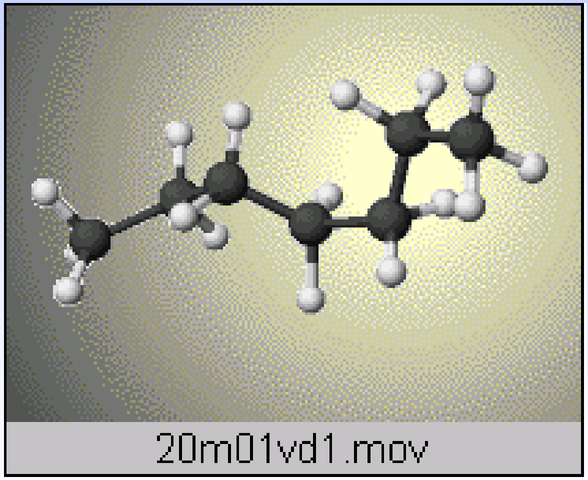
Entropy and Free Energy



How to predict if a reaction can occur, given enough time?

THERMODYNAMICS



How to predict if a reaction can occur at a reasonable rate?

KINETICS

Thermodynamics

- **If the state of a chemical system is such that a rearrangement of its atoms and molecules would decrease the energy of the system---**
- **AND the K is greater than 1,**
- **then this is a product-favored system.**
- **Most product-favored reactions are exothermic**

—but this is not the only criterion

Thermodynamics

- **Both product- and reactant-favored reactions can proceed to equilibrium in a spontaneous process.**

  $\mathrm{AgCl(s)}$ e $\mathrm{Ag^{+}(aq) + Cl^{-}(aq)}$
  $K = 1.8 \times 10^{-10}$

  Reaction is not product-favored, but it moves spontaneously toward equilibrium.

- **Spontaneous does not imply anything about time for reaction to occur.**

Thermodynamics and Kinetics

Diamond is **thermodynamically favored** to convert to graphite, but **not kinetically favored**.

Paper burns — a **product-favored** reaction. **Also kinetically favored** once reaction is begun.

Spontaneous Reactions

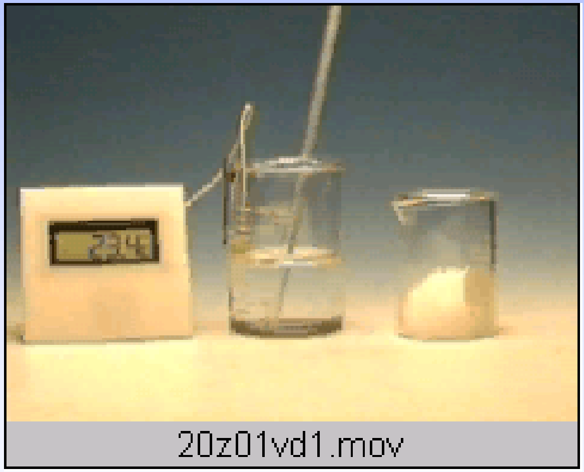
In general, spontaneous reactions are **exothermic**.

$Fe_2O_3(s) + 2\ Al(s) \dashrightarrow$
$2\ Fe(s) + Al_2O_3(s)$

$\Delta H = -848\ kJ$

Spontaneous Reactions

But many spontaneous reactions or processes are endothermic or even have $\Delta H = 0$.



$NH_4NO_3(s)$ + heat ---> $NH_4NO_3(aq)$

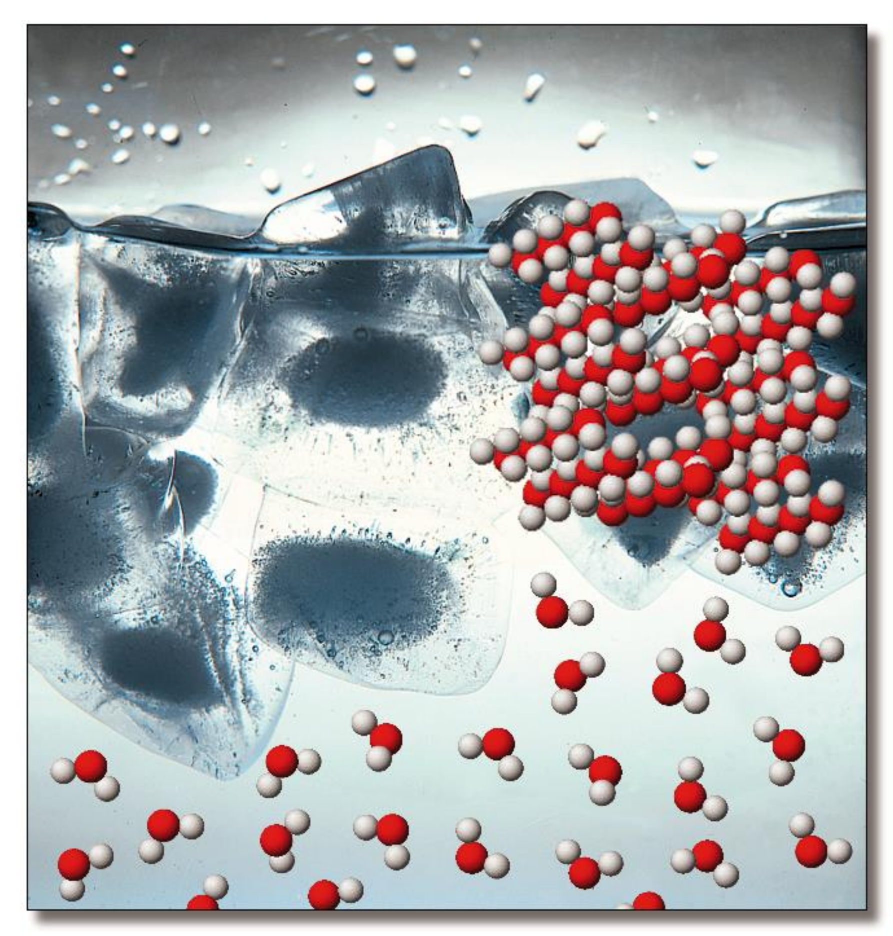
Entropy, S

One property common to spontaneous processes is that the final state is more **DISORDERED** or **RANDOM** than the original.

Spontaneity is related to an increase in randomness.

The thermodynamic property related to randomness is **ENTROPY, S**.

Reaction of K with water



The entropy of liquid water is greater than the entropy of solid water (ice) at 0˚ C.

Directionality of Reactions

How probable is it that reactant molecules will react?

PROBABILITY suggests that a spontaneous reaction will result in the dispersal

* of energy

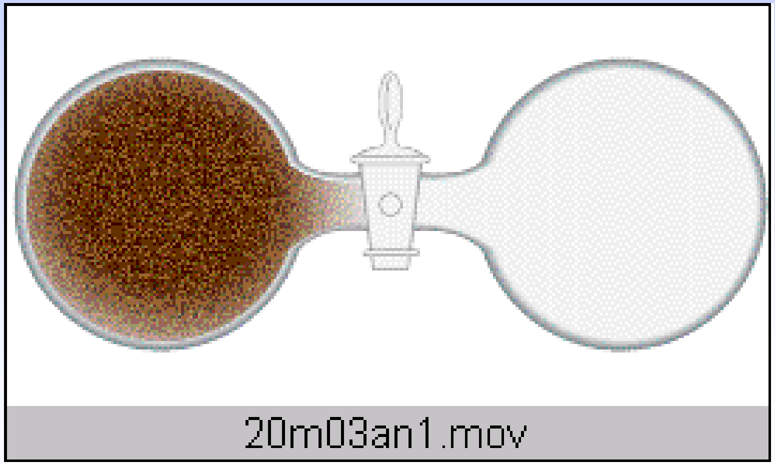
* or of matter

* or of energy & matter.

Directionality of Reactions

Probability suggests that a spontaneous reaction will result in the dispersal of energy or of matter or both.

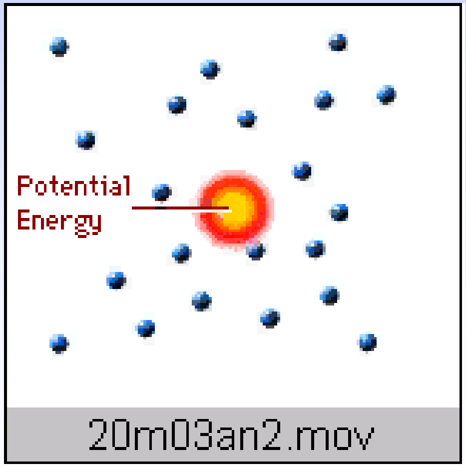
Matter Dispersal

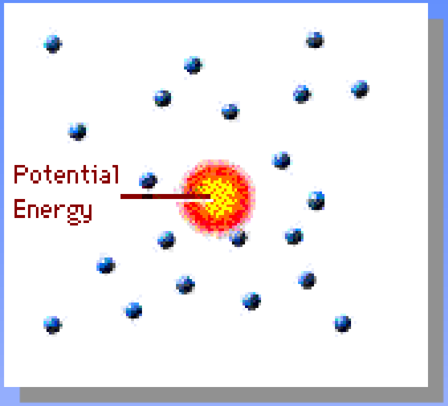


Directionality of Reactions

Probability suggests that a spontaneous reaction will result in the dispersal of energy or of matter or both.

Energy Dispersal





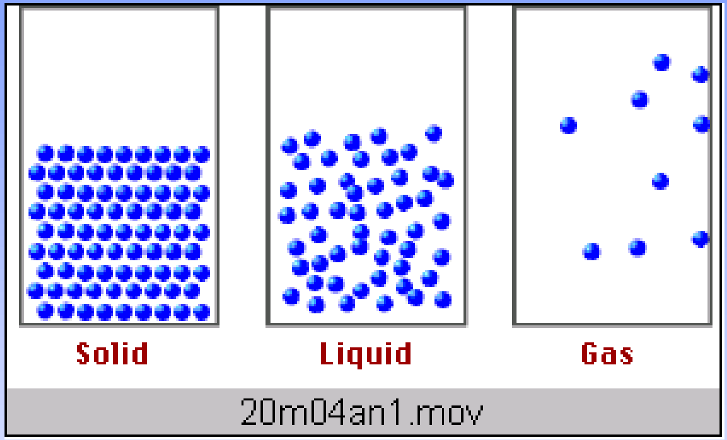
Directionality of Reactions Energy Dispersal

Exothermic reactions involve a release of stored chemical potential energy to the surroundings.

The stored potential energy starts out in a few molecules but is finally dispersed over a great many molecules.

The final state—with energy dispersed—is more probable and makes a reaction spontaneous.

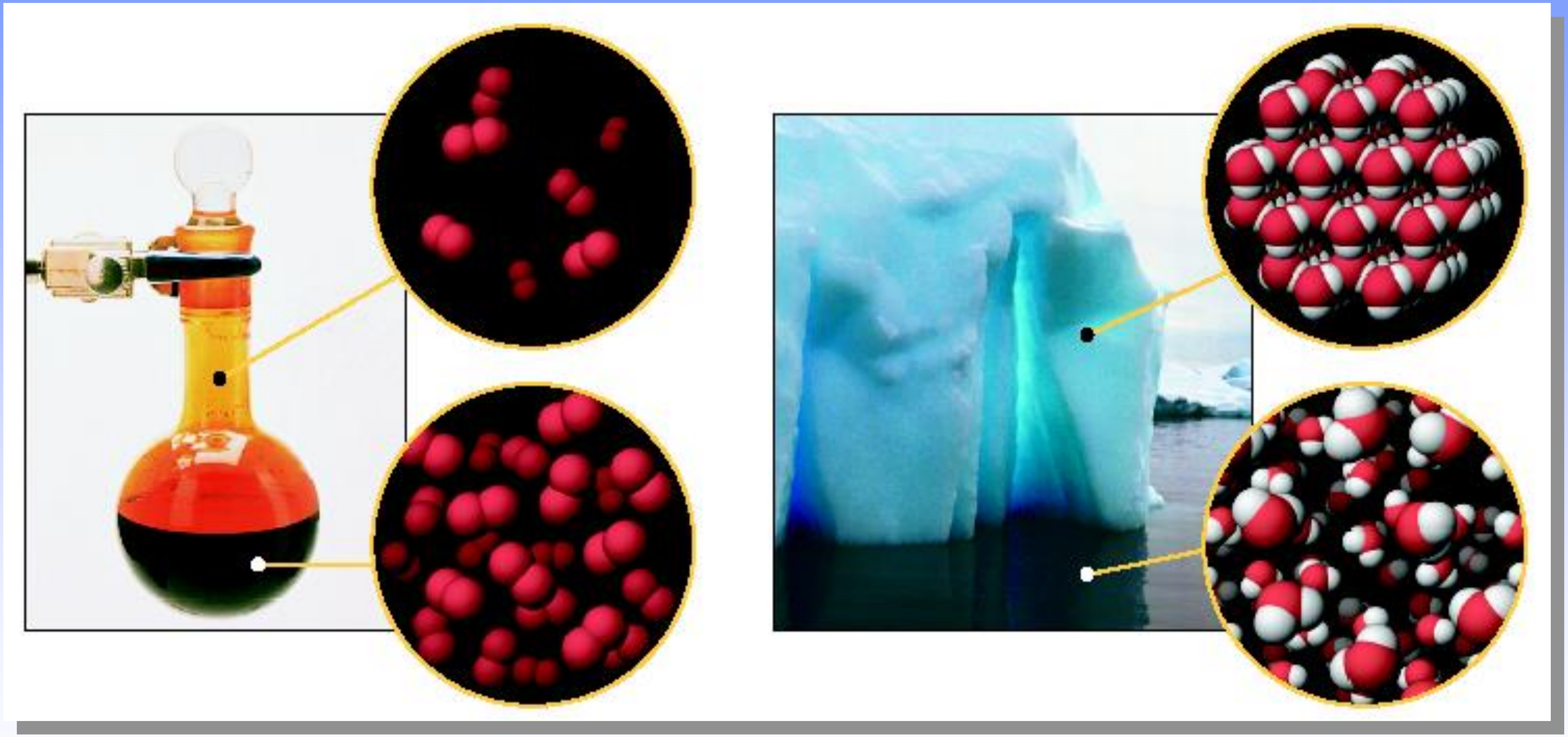
Entropy, S



	S^o (J/K•mol)
H_2O(liq)	69.95
H_2O(gas)	188.8

S (gases) > S (liquids) > S (solids)

Entropy and States of Matter



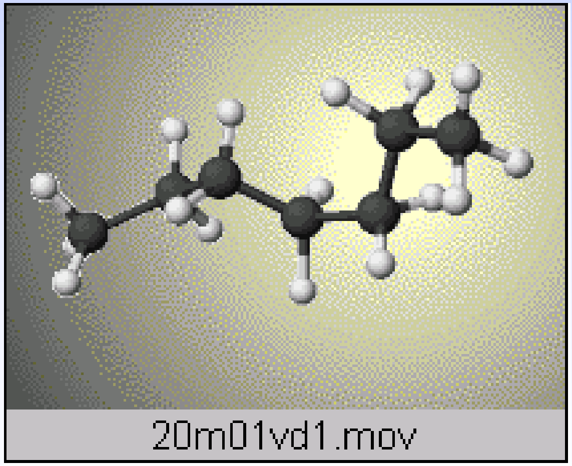
$S^\circ(Br_2\ \text{liq}) < S^\circ(Br_2\ \text{gas})$

$S^\circ(H_2O\ \text{sol}) < S^\circ(H_2O\ \text{liq})$

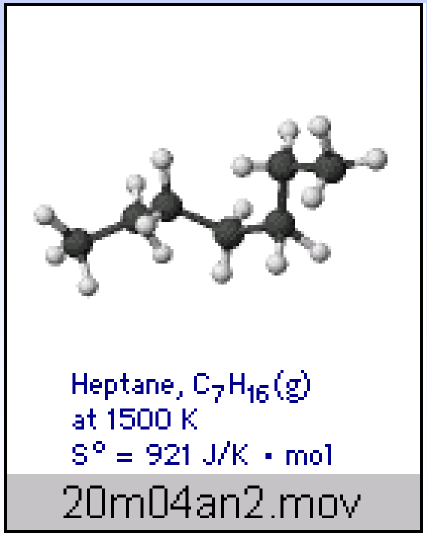
Entropy, S

Entropy of a substance increases with temperature.

Molecular motions of heptane, C_7H_{16}

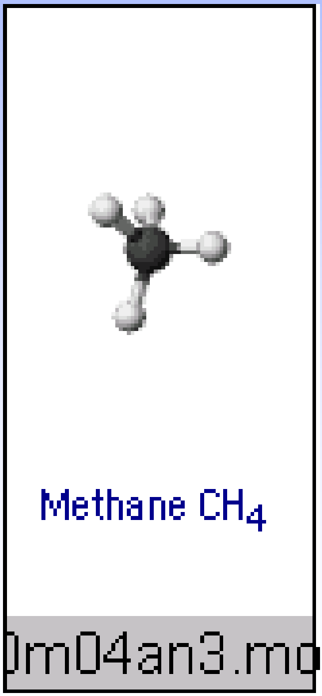


Molecular motions of heptane at different temps.

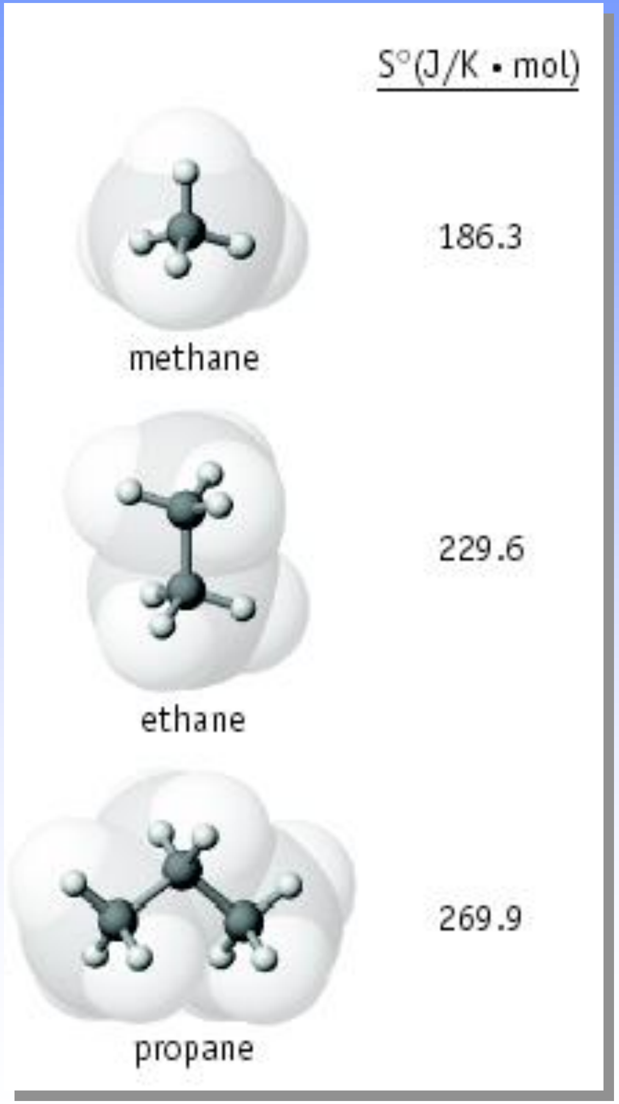


Entropy, S

Increase in molecular complexity generally leads to increase in S.



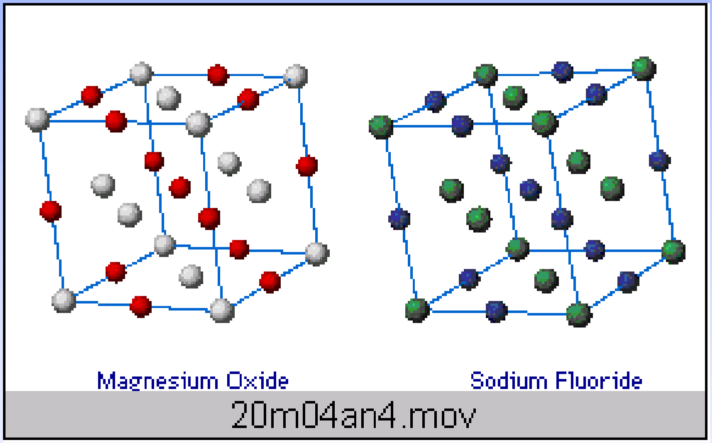
Methane CH_4



	S°(J/K • mol)
methane	186.3
ethane	229.6
propane	269.9

Entropy, S

Entropies of ionic solids depend on coulombic attractions.



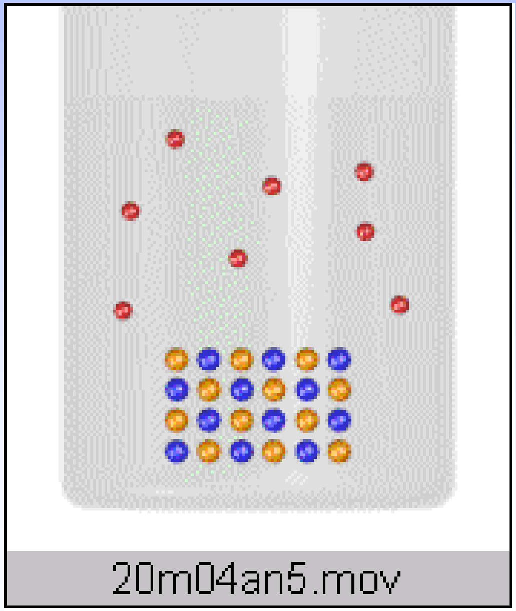
	S^o (J/K•mol)
MgO	26.9
NaF	51.5

Mg^{2+} & O^{2-}

Na^+ & F^-

Entropy, S

Entropy usually increases when a pure liquid or solid dissolves in a solvent.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Standard Molar Entropies

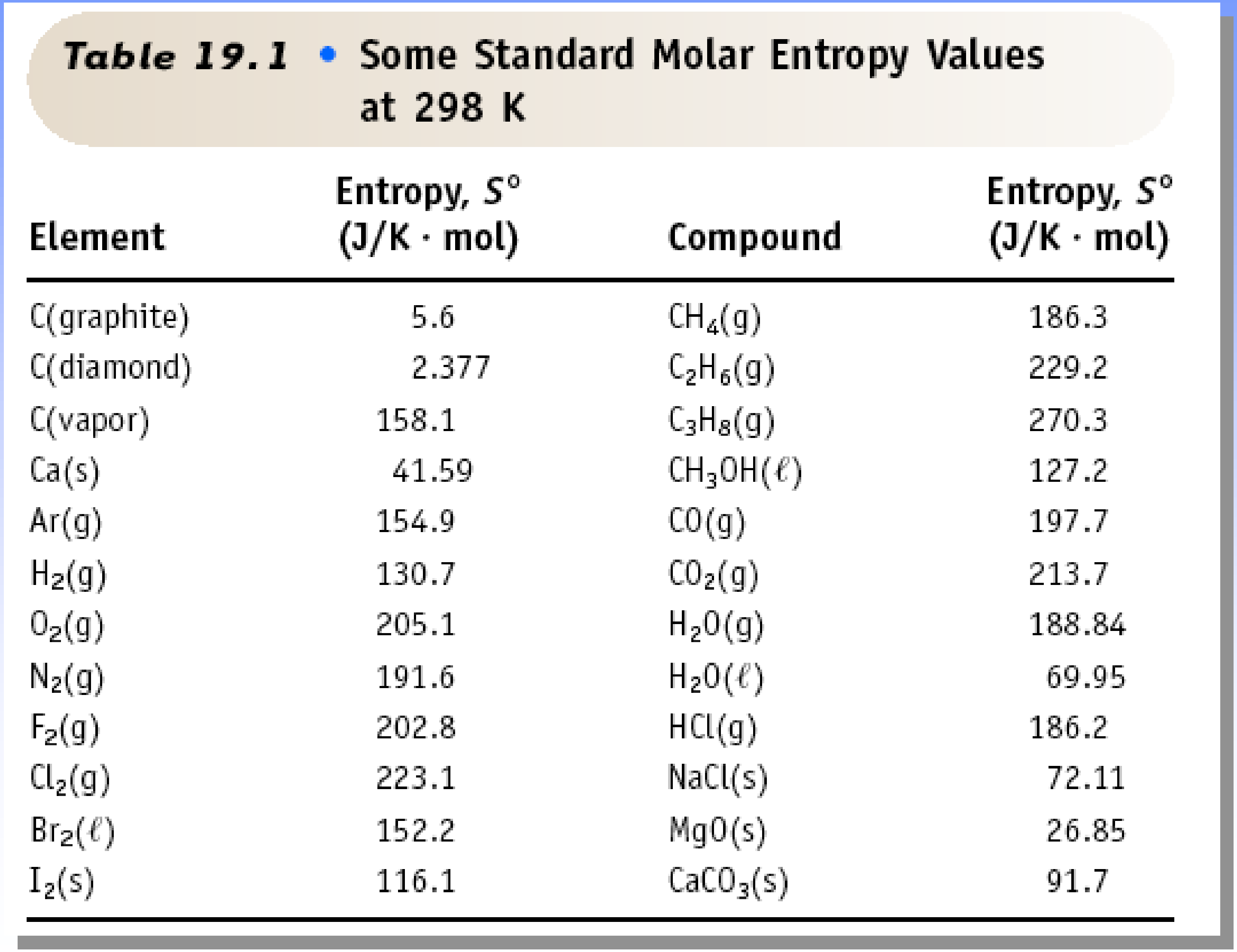


Table 19.1 • **Some Standard Molar Entropy Values at 298 K**

Element	Entropy, $S°$ (J/K · mol)	Compound	Entropy, $S°$ (J/K · mol)
C(graphite)	5.6	CH_4(g)	186.3
C(diamond)	2.377	C_2H_6(g)	229.2
C(vapor)	158.1	C_3H_8(g)	270.3
Ca(s)	41.59	$CH_3OH(\ell)$	127.2
Ar(g)	154.9	CO(g)	197.7
H_2(g)	130.7	CO_2(g)	213.7
O_2(g)	205.1	H_2O(g)	188.84
N_2(g)	191.6	$H_2O(\ell)$	69.95
F_2(g)	202.8	HCl(g)	186.2
Cl_2(g)	223.1	NaCl(s)	72.11
$Br_2(\ell)$	152.2	MgO(s)	26.85
I_2(s)	116.1	$CaCO_3$(s)	91.7

Entropy Changes for Phase Changes

For a phase change,

$$\Delta S = q/T$$

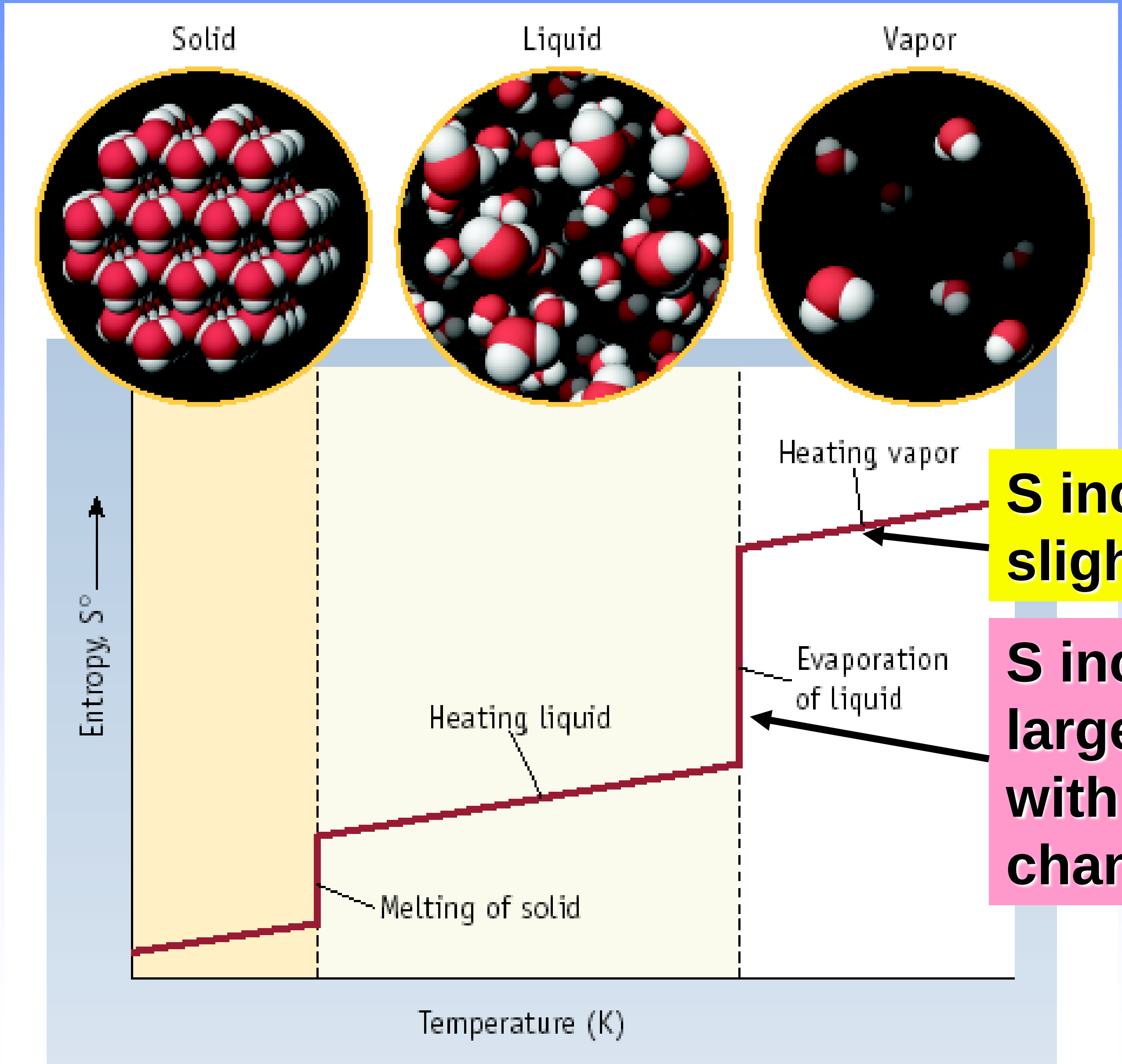
where q = heat transferred in phase change

For H_2O (liq) ---> $H_2O(g)$

$\Delta H = q = +40{,}700$ J/mol

$$\Delta S = \frac{q}{T} = \frac{40{,}700 \text{ J/mol}}{373.15 \text{ K}} = +109 \text{ J/K} \bullet \text{mol}$$

Entropy and Temperature



S increases slightly with T

S increases a large amount with phase changes

Calculating ΔS for a Reaction

$$\Delta S^o = \sum S^o\ (\text{products}) - \sum S^o\ (\text{reactants})$$

Consider $2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(liq)$

$\Delta S^o = 2\ S^o\ (H_2O)\ -\ [2\ S^o\ (H_2)\ +\ S^o\ (O_2)]$

$\Delta S^o = 2$ mol (69.9 J/K•mol) -
[2 mol (130.7 J/K•mol) +
1 mol (205.3 J/K•mol)]

$\Delta S^o = -326.9$ J/K

Note that there is a **decrease in S** because 3 mol of gas give 2 mol of liquid.

2nd Law of Thermodynamics

A reaction is spontaneous if ΔS for the universe is positive.

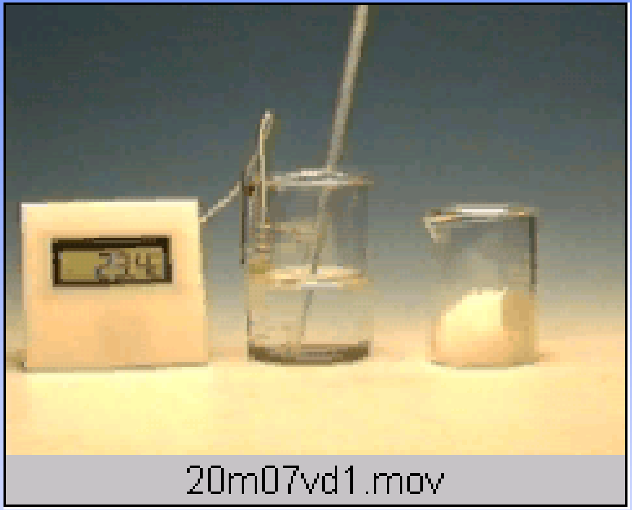
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$\Delta S_{universe} > 0$ for spontaneous process

First calc. entropy created by matter dispersal (ΔS_{system})

Next, calc. entropy created by energy dispersal ($\Delta S_{surround}$)

2nd Law of Thermodynamics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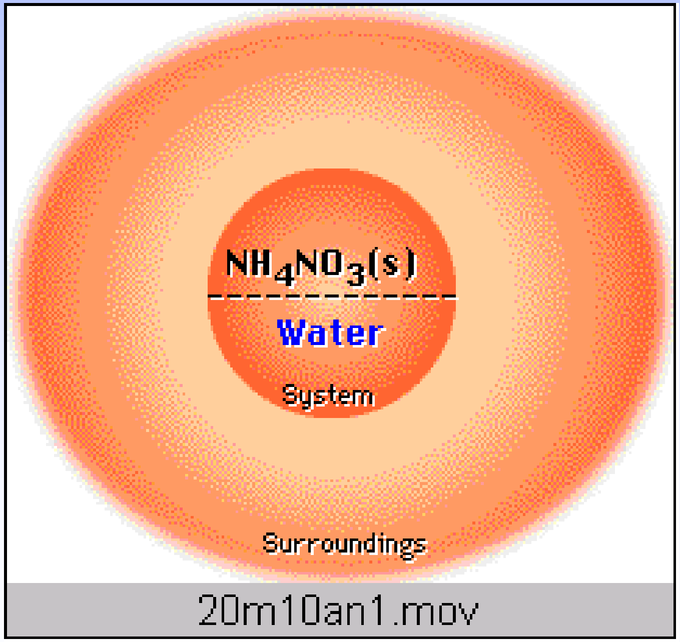
Dissolving NH_4NO_3 in water—an **entropy driven** process.



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$\Delta S_{universe} =$

$\Delta S_{system} + \Delta S_{surroundings}$

2nd Law of Thermodynamics

$2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

$\Delta S^o_{system} = -326.9 \text{ J/K}$

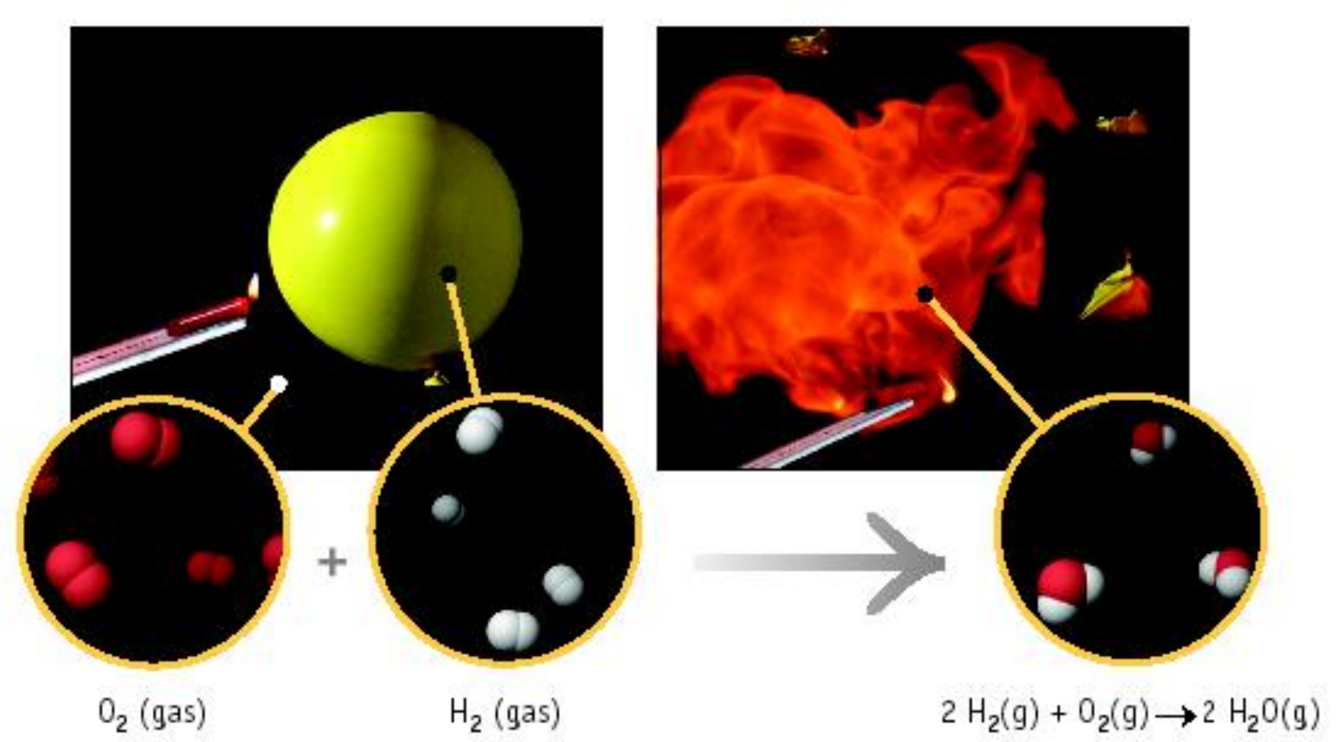
$$\Delta S^o_{surroundings} = \frac{q_{surroundings}}{T} = \frac{-\Delta H_{system}}{T}$$

Can calc. that $\Delta H^o_{rxn} = \Delta H^o_{system} = -571.7 \text{ kJ}$

$$\Delta S^o_{surroundings} = \frac{-\ (-571.7 \text{ kJ})(1000 \text{ J/kJ})}{298.15 \text{ K}}$$

$\Delta S^o_{surroundings} = +1917 \text{ J/K}$

2nd Law of Thermodynamics



$2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

$\Delta S^o_{system} = -326.9$ J/K

$\Delta S^o_{surroundings} = +1917$ J/K

$\Delta S^o_{universe} = +1590.$ J/K

- The entropy of the universe is increasing, so the reaction is product-favored.

Spontaneous or Not?

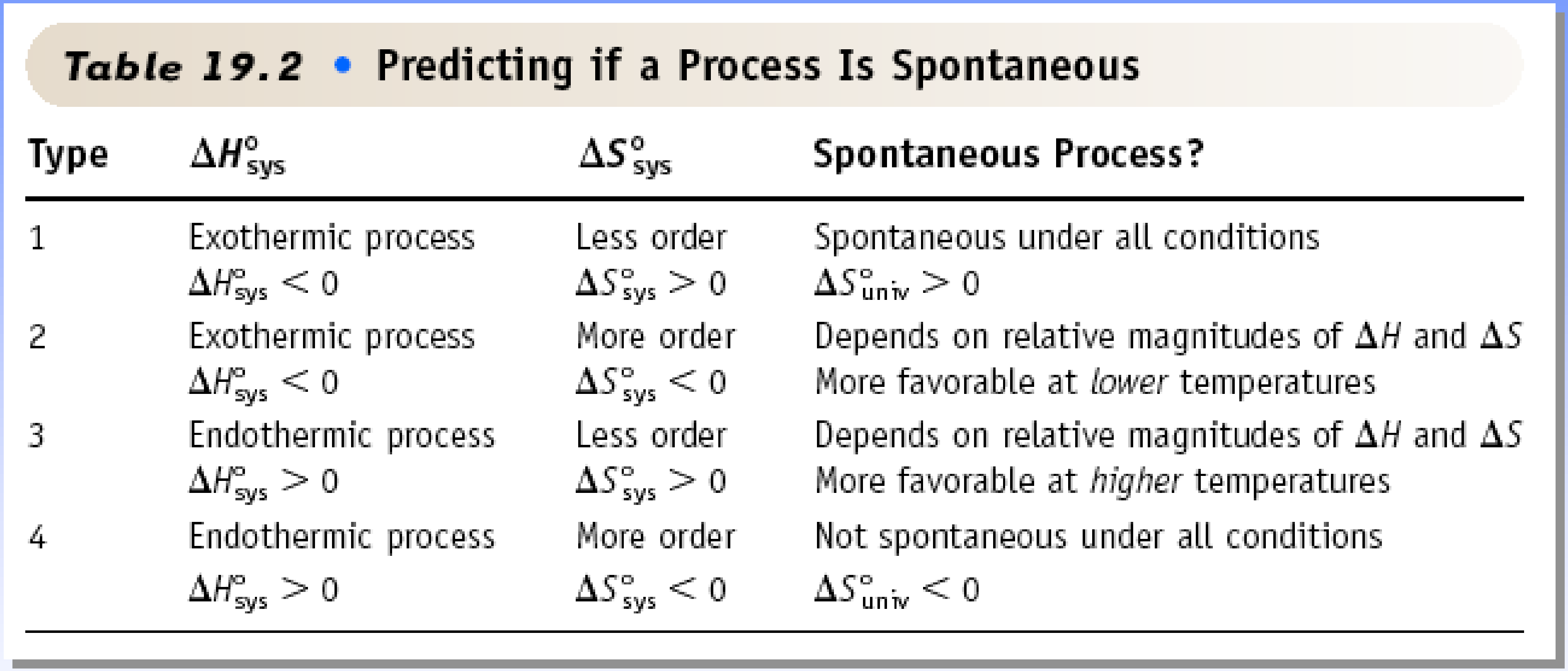


Table 19.2 • Predicting if a Process Is Spontaneous

Type	ΔH°_{sys}	ΔS°_{sys}	Spontaneous Process?
1	Exothermic process $\Delta H^\circ_{sys} < 0$	Less order $\Delta S^\circ_{sys} > 0$	Spontaneous under all conditions $\Delta S^\circ_{univ} > 0$
2	Exothermic process $\Delta H^\circ_{sys} < 0$	More order $\Delta S^\circ_{sys} < 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at *lower* temperatures
3	Endothermic process $\Delta H^\circ_{sys} > 0$	Less order $\Delta S^\circ_{sys} > 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at *higher* temperatures
4	Endothermic process $\Delta H^\circ_{sys} > 0$	More order $\Delta S^\circ_{sys} < 0$	Not spontaneous under all conditions $\Delta S^\circ_{univ} < 0$

Remember that $-\Delta H^\circ_{sys}$ is proportional to ΔS°_{surr}

An exothermic process has $\Delta S^\circ_{surr} > 0$.