

ENTROPY

A *spontaneous* process has a tendency to occur without being driven by an external influence; does not have to be fast

Entropy is a measure of disorder (probability?)

Entropy is a state function

The 2nd law:

The entropy of an isolated system increases in the course of any spontaneous change

Changes in physical state and entropy (changes)

- During the phase transition, the temperature remains constant
- At the temperature of phase transition, the transfer of heat is reversible

Since we know that

For $P = \text{const}$, $q_{\text{transition}} = \Delta H_{\text{transition}}$

Ergo: $\Delta S_{\text{transition}} = \Delta H_{\text{transition}} / T_{\text{transition}}$

$\Delta S^0_{\text{transition}}$ – standard entropy of transition ($\text{J mol}^{-1} \text{K}^{-1}$)

Trouton's "rule"

Trouton's "rule" is an observation that for many liquids, the entropy of vaporization is ca. 85 J·K/mol

TABLE 7.1 Standard Entropy of Vaporization at the Normal Boiling Point*

Liquid	Boiling point (K)	$\Delta S_{\text{vap}}^{\circ}$ (J·K ⁻¹ ·mol ⁻¹)
acetone	329.4	88.3
ammonia	239.7	97.6
argon	87.3	74
benzene	353.2	87.2
ethanol	351.5	124
helium	4.22	20.
mercury	629.7	94.2
methane	111.7	73
methanol	337.8	105
water	373.2	109

*The normal boiling point is the boiling temperature at 1 atm.

The Third Law of Thermodynamics

The entropies of all perfect crystal approach zero as the absolute temperature approaches zero

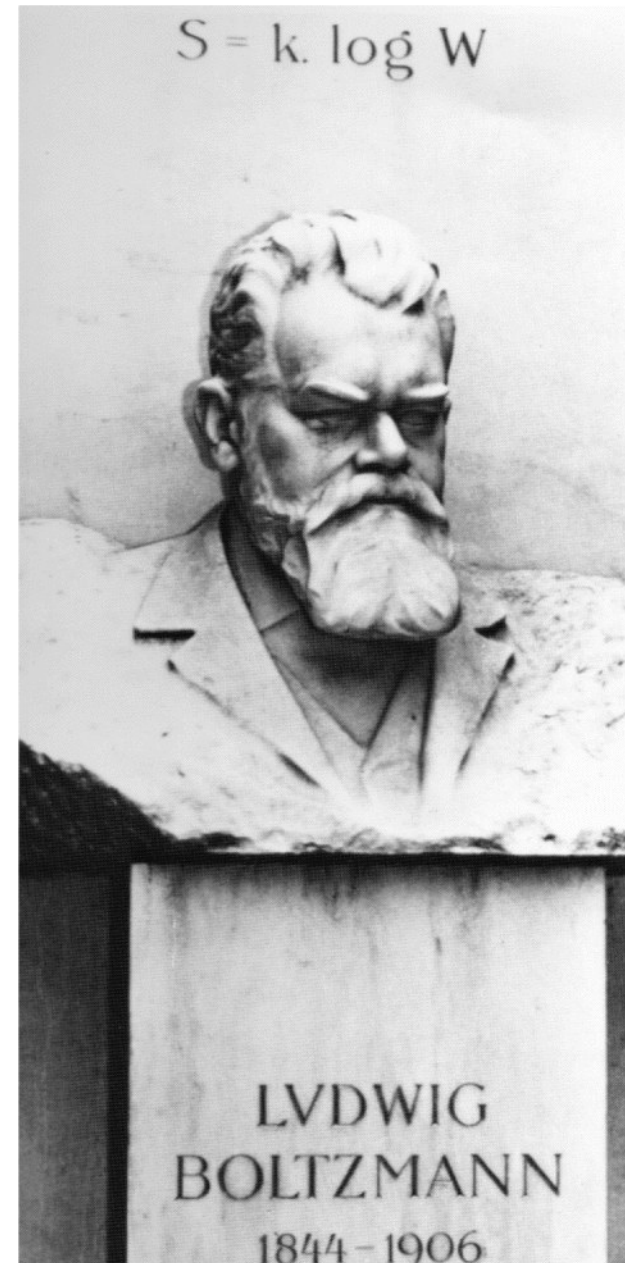
The key word is “approaches”.

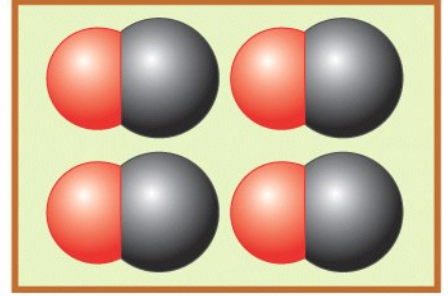
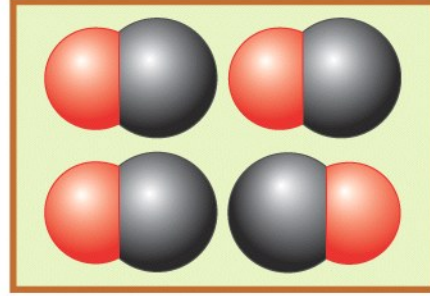
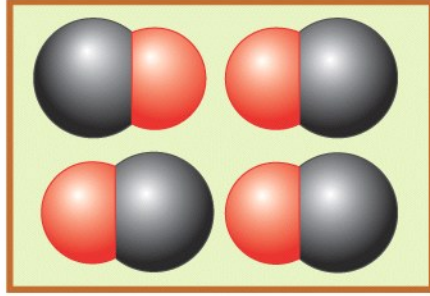
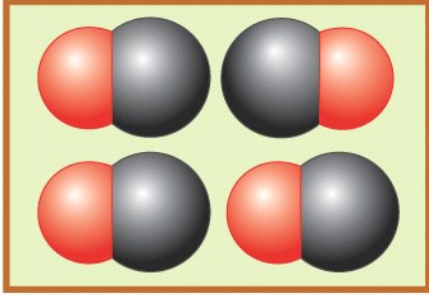
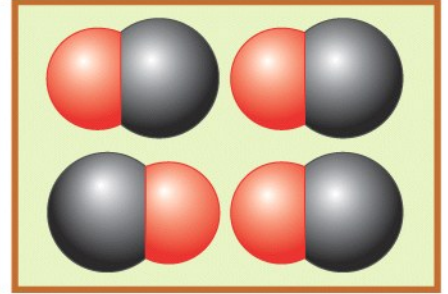
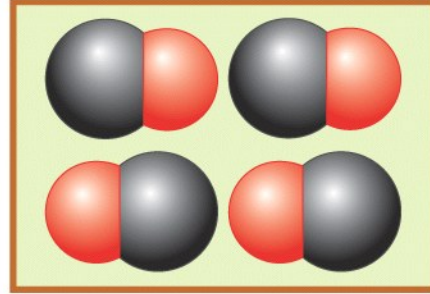
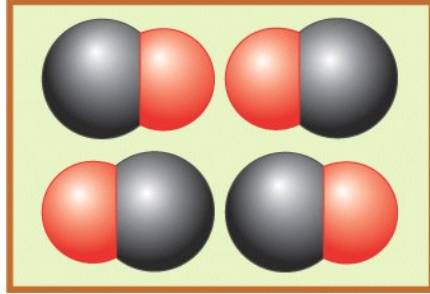
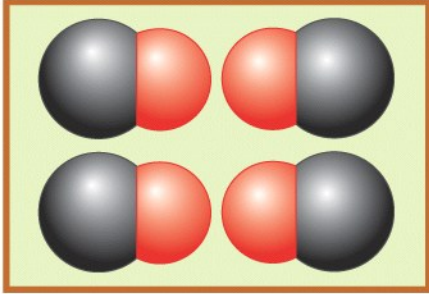
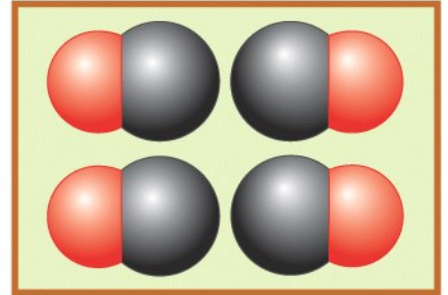
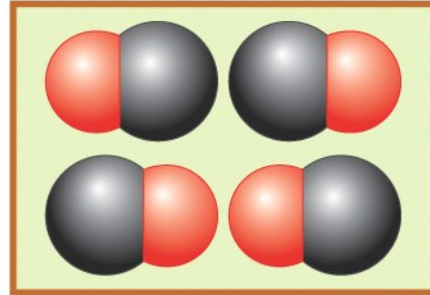
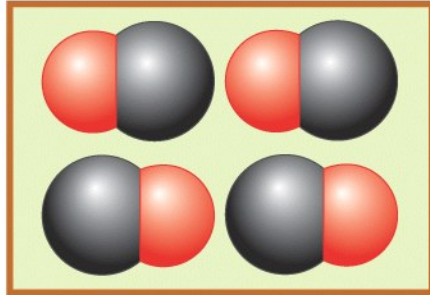
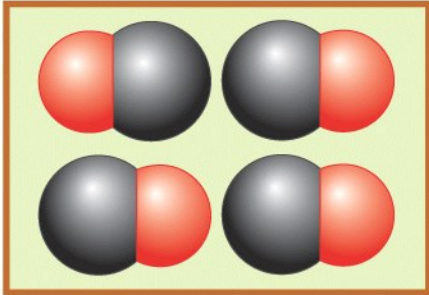
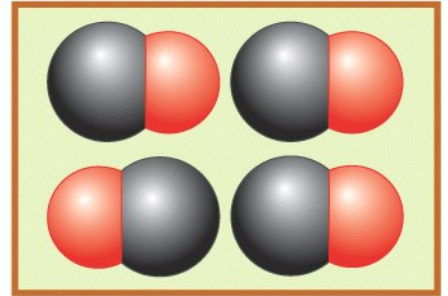
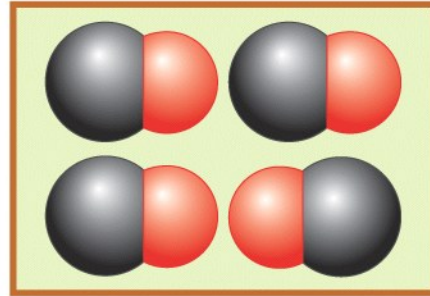
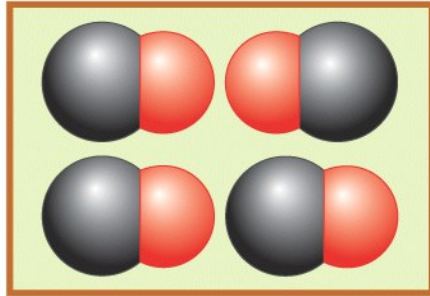
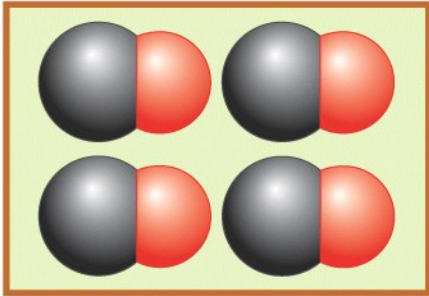
Statistical entropy

$$S = k \ln(W),$$

where W is the number of different microstates for the macrostate

The statistical definition of entropy is equivalent to that derived from macroscopic observations

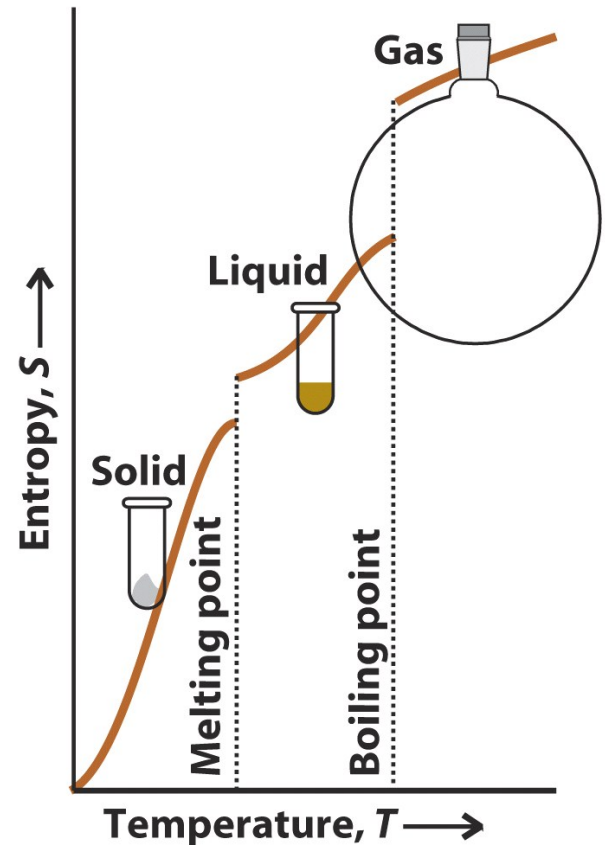


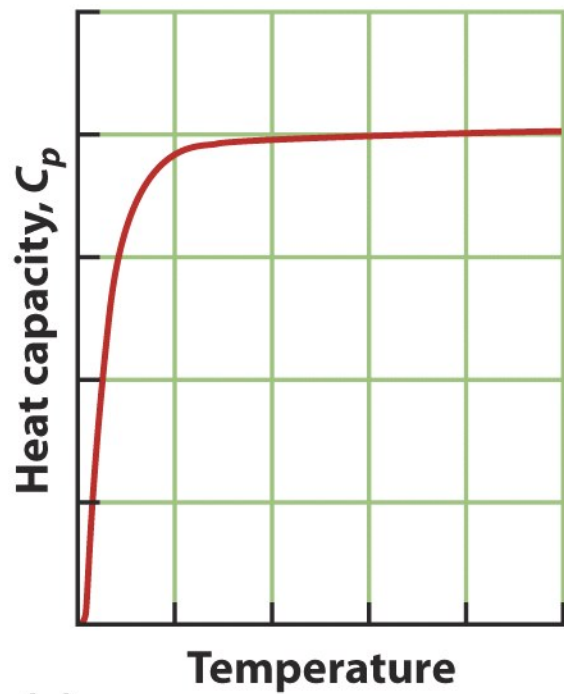


Standard molar entropy (S^0_m)

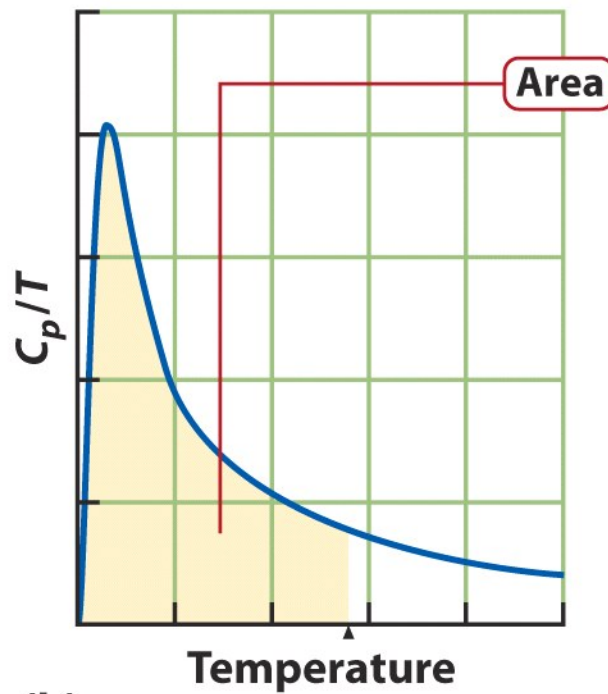
$$S(T) = S(0) + \Delta S(0 \rightarrow T)$$

$\Delta S(0 \rightarrow T)$ must account for phase transitions

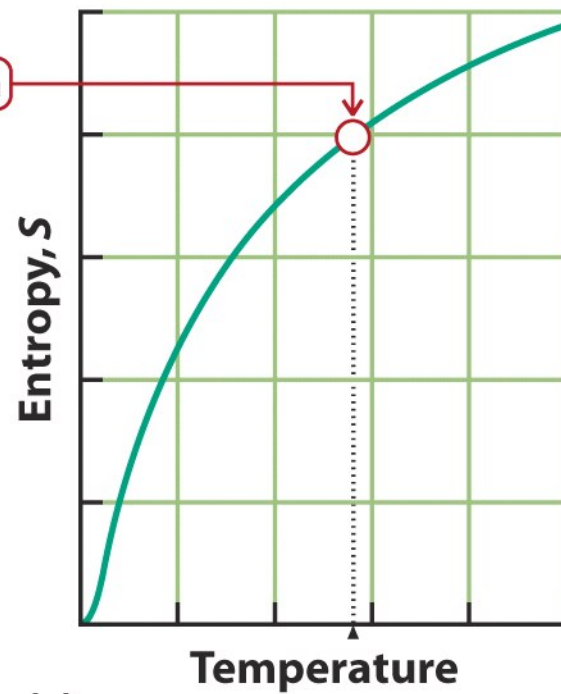




(a)



(b)



(c)

Table 8.2 Standard Molar Entropy of Water at Various Temperatures

Phase	Temperature (°C)	S_m° (J·K ⁻¹ ·mol ⁻¹)
solid	-273 (0 K)	3.4
	0	43.2
liquid	0	65.2
	20	69.6
	50	75.3
	100	86.8
vapor	100	196.9
	200	204.1

TABLE 8.3 Standard Molar Entropies at 25°C (J·K⁻¹·mol⁻¹)*

Gases	S_m°	Liquids	S_m°	Solids	S_m°
ammonia, NH ₃	192.4	benzene, C ₆ H ₆	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO ₂	213.7	ethanol, C ₂ H ₅ OH	160.7	calcium carbonate, CaCO ₃ [†]	92.9
hydrogen, H ₂	130.7	water, H ₂ O	69.9	diamond, C	2.4
nitrogen, N ₂	191.6			graphite, C	5.7
oxygen, O ₂	205.1			lead, Pb	64.8

*Additional values are given in Appendix 2A.

[†]Calcite.

Standard reaction entropy

$$\Delta S_{\text{rxn}}^0 = \sum n S_m^0(\text{products}) - \sum n S_m^0(\text{reactants})$$

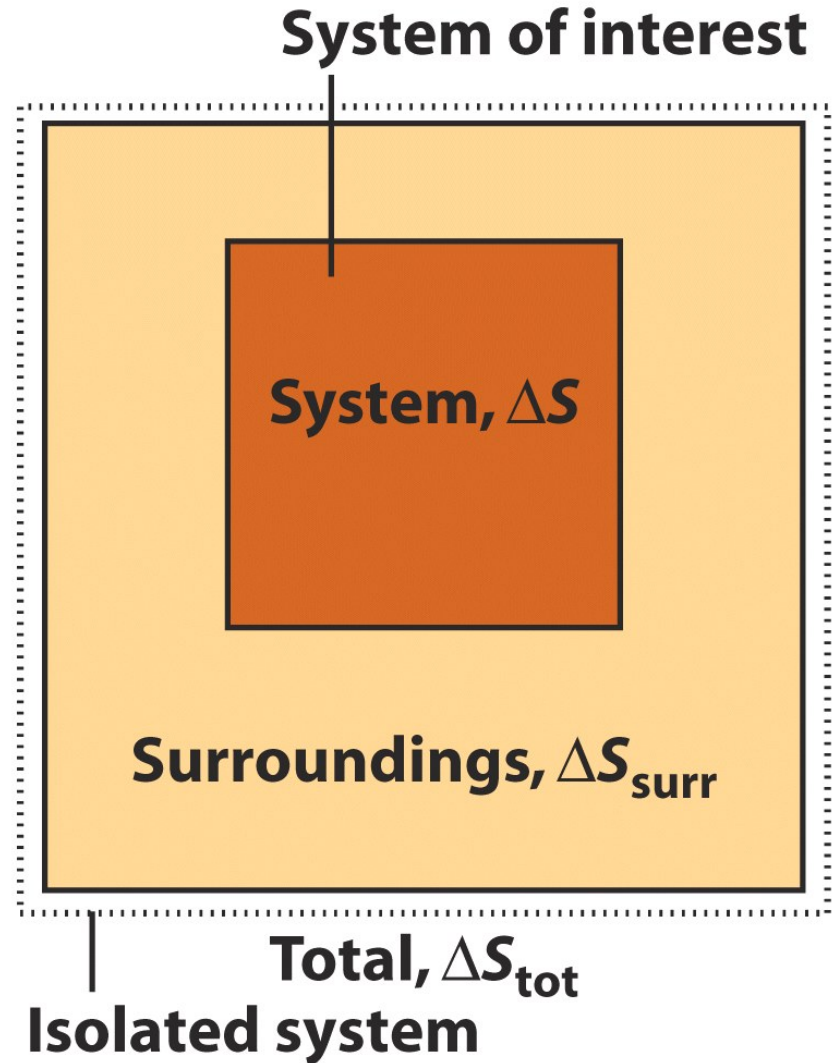
For reactions in which the amount of gas increases, ΔS_{rxn}^0 is usually positive (and vice versa).

Also, generally, the increase in the number of particles in (ideal) solution or gas phase leads to increase in entropy.

Global changes in entropy

The 2nd law refers to the isolated system. In order to determine whether the process is spontaneous, we need to know the change in entropy for both the system and the surroundings.

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{surr}}$$



(Dynamic) Equilibrium

A system is at equilibrium when it has no tendency to change in either direction. Microscopic processes continue, but there is no net change.

In other words, neither the forward nor the reverse process is spontaneous, which means....

$$\Delta S_{\text{tot}} = 0$$

Gibbs free energy

Allows us to determine spontaneity considering the system alone

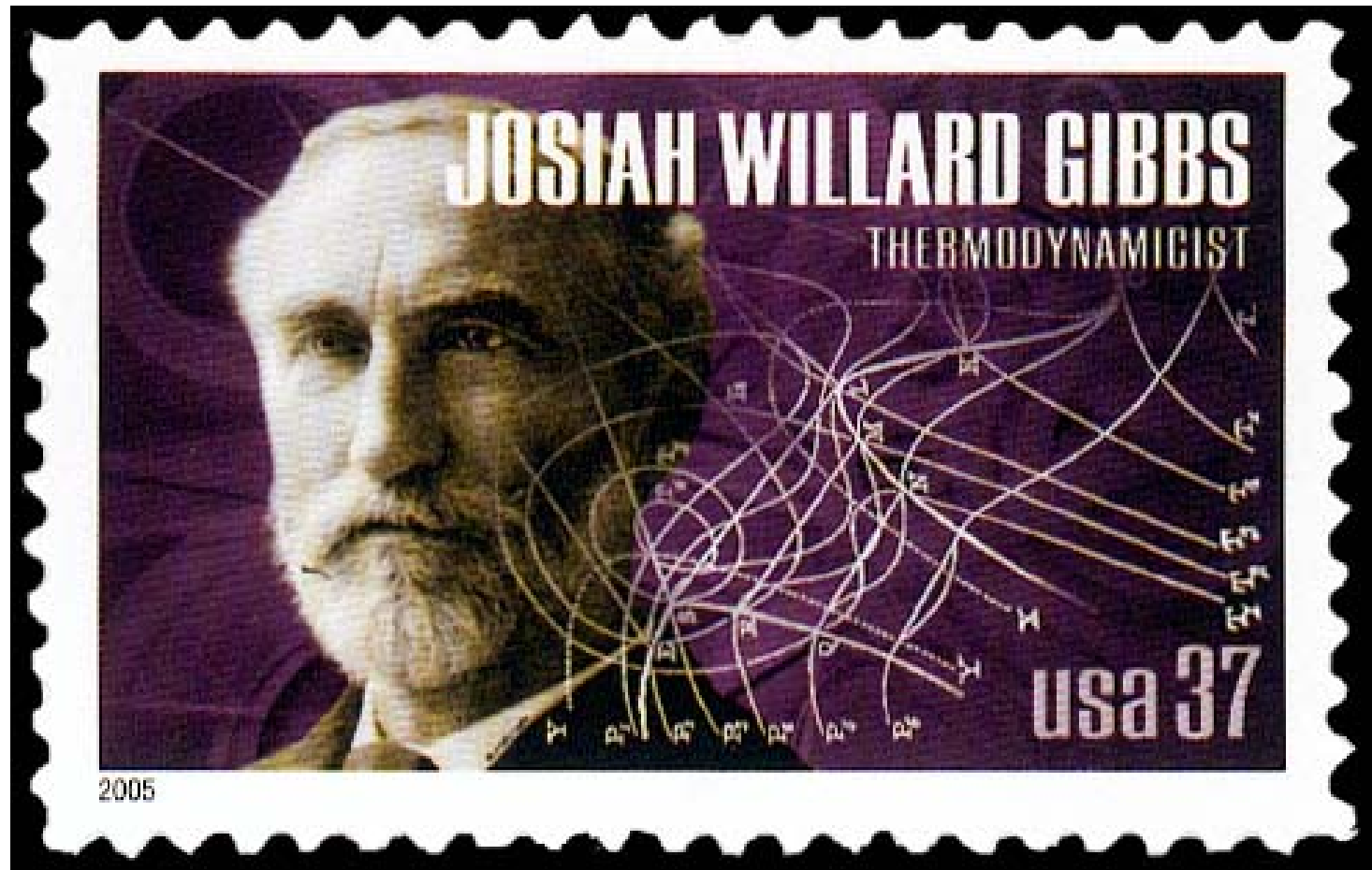
May be thought to quantify the maximum amount of non-expansion work the system can perform

Is a state function

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \quad (T, P = \text{const})$$

$\Delta G < 0$ corresponds to a spontaneous process



1839 – 1903

TABLE 7.5 Factors That Favor Spontaneity

change	Entropy change	Spontaneous?
exothermic ($\Delta H < 0$)	increase ($\Delta S > 0$)	yes, $\Delta G < 0$
exothermic ($\Delta H < 0$)	decrease ($\Delta S < 0$)	yes, if $ T\Delta S < \Delta H $, $\Delta G < 0$
endothermic ($\Delta H > 0$)	increase ($\Delta S > 0$)	yes, if $T\Delta S > \Delta H$, $\Delta G < 0$
endothermic ($\Delta H > 0$)	decrease ($\Delta S < 0$)	no, $\Delta G > 0$

Sometimes enthalpy “competes” with entropy

Spontaneity or favorability of a process may change with temperature

Gibbs free energy of reaction and standard Gibbs free energy of formation

$$\Delta G^0_{\text{rxn}} = \sum n G^0_{\text{m}}(\text{products}) - \sum n G^0_{\text{m}}(\text{reactants})$$

Standard Gibbs free energy of formation for a compound is the standard Gibbs free energy of a reaction to produce 1 mole of said compound from elemental compounds in their standard state.

Units of J/(mol).

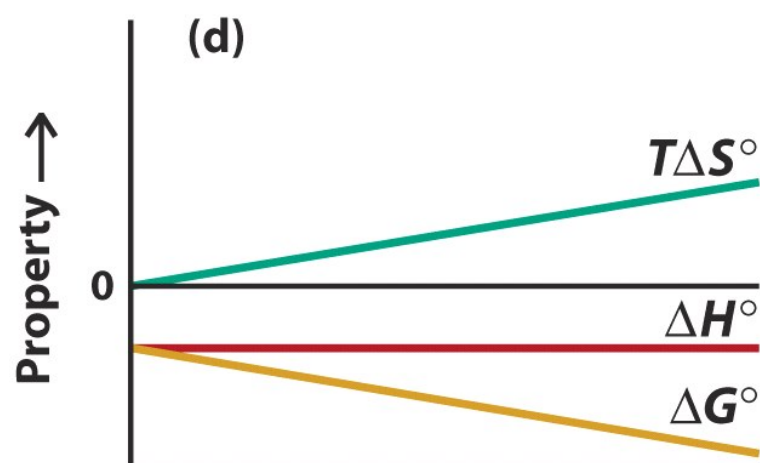
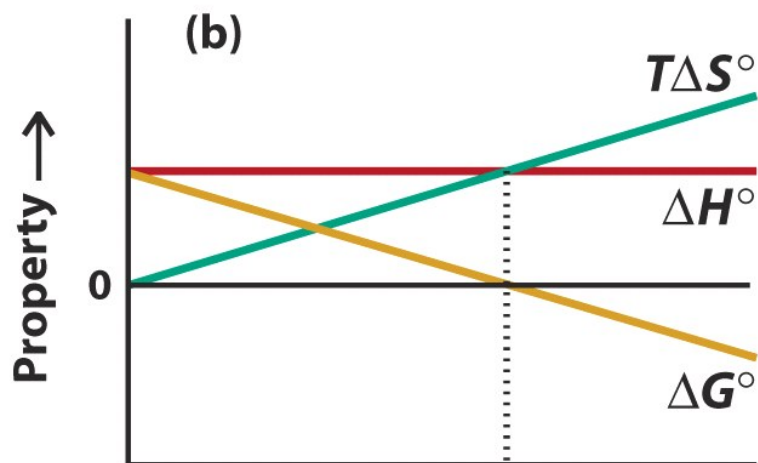
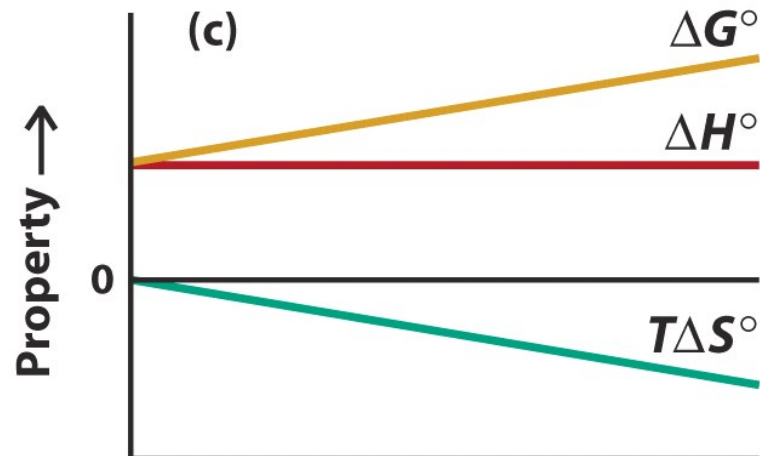
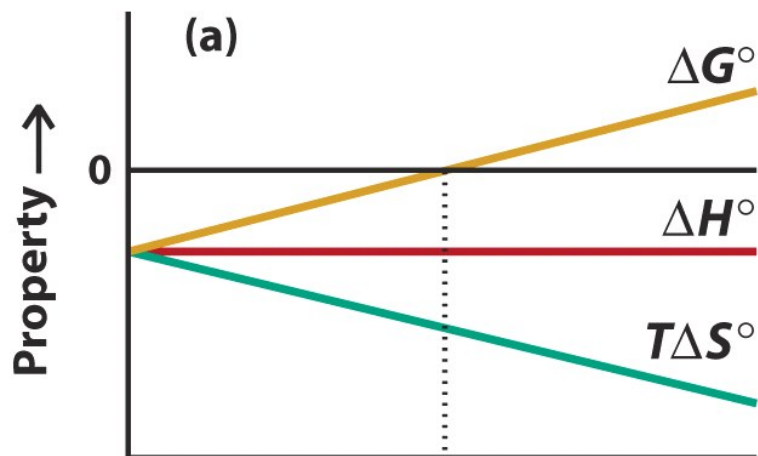
$$\Delta G^0_{\text{rxn}} = \sum n G^0_{\text{f}}(\text{products}) - \sum n G^0_{\text{f}}(\text{reactants})$$

Gibbs energy and non-expansion work

Gibbs energy of a closed system is the measure of the energy “free” to do non-expansion work (e.g., mechanical, electrical, etc.).

The change in free energy of a process (ΔG) is the maximum non-expansion work this process can do.

Effect of temperature on ΔG



Temperature, $T \rightarrow$