

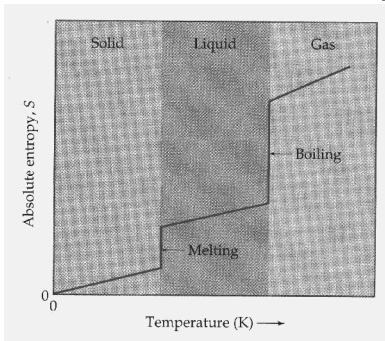
THIRD LAW OF THERMODYNAMICS

As a system approaches absolute zero of temperature all processes cease and the entropy of the system approaches a minimum value.

THIRD LAW OF THERMODYNAMICS

The entropy of a pure crystalline substance at absolute zero is zero.

$$S(0\text{ K}) = 0 \Rightarrow \text{perfect order}$$



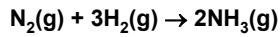
Entropy increases for $s \rightarrow l \rightarrow g$

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 ₂ O(g)	188.8
NH ₃ (g)	192.5
CH ₃ OH(g)	237.6
C ₆ H ₆ (g)	269.2
Liquids	
H ₂ O(l)	69.9
CH ₃ OH(l)	126.8
C ₆ H ₆ (l)	172.8
Solids	
Fe(s)	27.2
FeCl ₃ (s)	142.3
NaCl(s)	72.3

EXAMPLE

Calculate ΔS° for the synthesis of ammonia from N₂(g) and H₂(g):



Calculation of ΔS for the surroundings

For a process that occurs at constant temperature and pressure, the entropy change of the surroundings is:

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad (\text{T \& P constant})$$

GIBB'S FREE ENERGY (G)



FIGURE 16.21 Josiah Willard Gibbs (1839–1903).

- Defined as: $G = H - TS$
- state function
 - extensive property

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

At constant T and P:

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

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

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad (\text{at constant T \& P})$$

We know:

Spontaneous process: $\Delta S_{\text{univ}} > 0$

Process at equilibrium: $\Delta S_{\text{univ}} = 0$

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

Therefore:

Spontaneous process: $\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$

Process at equilibrium: $\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} = 0$

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

Spontaneity involves

Spontaneity is favoured by increasing ΔS and ΔH is large and negative.

ΔG allows us to predict whether a process is spontaneous or not (under constant temperature and pressure conditions):

$\Delta G < 0 \Rightarrow$ spontaneous in forward direction

$\Delta G > 0 \Rightarrow$ non-spontaneous in forward direction/spontaneous in reverse direction

$\Delta G = 0 \Rightarrow$ at equilibrium

Standard free energy (ΔG°)

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

Standard states:

Gas	-	1 atm
Solid	-	pure substance
Liquid	-	pure liquid
Solution	-	Concentration = 1M

$\Delta G_f^\circ = 0$ kJ/mol for elements in their standard states

Tabulated data of ΔG_f° can be used to calculate standard free energy change for a reaction as follows:

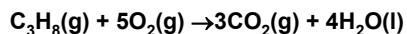
$$\Delta G^\circ = \sum \eta \Delta G_f^\circ(\text{products}) - \sum \eta \Delta G_f^\circ(\text{reactants})$$

Stoichiometric coefficients

Substance	(kJ mol ⁻¹)	S _m ^o (J K ⁻¹ mol ⁻¹)	(kJ mol ⁻¹)	Substance	(kJ mol ⁻¹)	S _m ^o (J K ⁻¹ mol ⁻¹)	(kJ mol ⁻¹)
AgS	0	+42.6	0	I ₂ (s)	0	+116.1	-11.6
AgCl(s)	-127.1	+96.2	-109.8	I ₂ (g)	+62.4	+260.6	+19.4
Al(s)	0	+28.32	0	MgO(s)	-601.5	+27.0	-599.2
AlCl ₃ (s)	-704.2	+110.7	-698.8	MnO ₂ (s)	-520.0	+53.1	-465.2
Al ₂ O ₃ (s)	-1669.8	+51.0	-1576.5	N ₂ (g)	0	+191.5	0
Br ₂ (l)	0	+152.2	0	N ₂ O ₄ (g)	+9.3	+304.2	+97.8
BrF ₃ (g)	-255.6	+292.4	-229.5	Na(s)	0	+51.3	0
Cl(g)	+716.7	+158.0	+671.3	NaF(s)	-569.0	+51.3	-546.3
Cl ₂ (g)	0	+5.8	0	NaCl(s)	-411.1	+72.4	-384.3
Cl ₂ (diamond)	+1.9	+2.4	+2.9	NaBr(s)	-361.1	+87.2	-348.1
CO(g)	-110.5	+197.8	-137.2	Na(s)	-287.8	+98.5	-282.4
CO ₂ (g)	-393.5	+213.7	-394.4	NaOH(s)	-425.6	+64.5	-379.5
CH ₄ (g)	-74.5	+186.1	-50.8	NH ₃ (g)	-46.2	+192.7	-16.4
C ₂ H ₆ (g)	-103.8	+289.9	-23.4	N ₂ H ₄ (l)	+50.6	+121.2	+149.2
Ca(s)	0	+41.4	0	NO(g)	+90.3	+210.6	+86.6
CaO(s)	-635.1	+38.1	-603.5	NO ₂ (g)	+33.2	+240.0	+51.3
CaCO ₃ (s)(calcite)	-1206.9	+92.9	-1128.8	HNO ₃ (l)	-174.1	+155.6	-80.8
Cl ₂ (g)	0	+223.0	0	O ₂ (g)	0	+205.0	0
Ca(s)	0	+33.2	0	O ₃ (g)	+142.7	+238.8	+163.2
F ₂ (g)	0	+202.7	0	P(s)(white)	0	+41.1	0
Fe(s)	0	+27.3	0	P ₄ (s)(s)	-3010.0	+231.0	-2724.0
Fe ₂ O ₃ (s)(hematite)	-824.2	+67.4	-742.2	PCl ₃ (g)	-287.0	+311.7	-267.8
Hg	+218.0	+114.6	+203.3	PCl ₅ (g)	-374.9	+364.5	-305.0
H ₂ (g)	0	+130.6	0	PbCO ₃ (s)	-277.4	+86.6	-217.4
HCl(g)	-92.3	+186.8	-95.3	Si(s)(orthorhombic)	0	+32.0	0
HF(g)	-271.1	+173.8	-273.2	H ₂ S(g)	-20.6	+205.6	-33.4
Hl(g)	+26.4	+206.5	+1.6	SiO ₂ (s)(quartz)	-910.7	+41.5	-856.3
HBr(g)	-36.4	+198.6	-53.5	SiCl ₄ (l)	-687.0	+239.7	-619.9
HCN(g)	+135.1	+201.7	+124.7	SO ₂ (g)	-296.8	+248.1	-300.2
H ₂ O(g)	-241.8	+188.7	-228.6	SO ₃ (g)	-395.7	+256.6	-371.1
H ₂ O(l)	-285.8	+70.0	-237.2	Zn(s)	0	+41.8	0
H ₂ C ₂ (l)	-187.8	+109.6	-120.4	ZnO(s)	-350.5	+43.6	-320.5
H ₂ (l)	0	+75.6	0				

EXAMPLE

The combustion of propane gas occurs as follows:



Using thermodynamic data for ΔG° , calculate the standard free energy change for the reaction at 298 K.
