Practice problem

Which substance has the higher entropy under standard conditions at 25 ˚C? Explain your reasoning.

- NO_2 (g) or N_2O_4 (g)
- I_2 (g) or I_2 (s)

- NO_2 is a smaller molecule than N_2O_4 (more order in N_2O_4) so **N_2O_4 has the higher entropy** (more possible microstates)
- The solid state has more order than the gas state, so **I_2 (g) has the higher entropy**

Practice problem

Using standard molar entropies, calculate the standard entropy changes in the following processes

- $C_2H_5OH\ (l) \rightarrow C_2H_5OH\ (g)$
- $N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$

Substance	S˚ (J K^{-1} mol^{-1})
C_2H_5OH (l)	160.7
C_2H_5OH (g)	282.70
N_2 (g)	191.56
H_2 (g)	130.7
NH_3 (g)	192.77

- $\Delta S^\circ = S^\circ_{products} - S^\circ_{reactants} = 282.70\ J\ K^{-1}\ mol^{-1} - 160.7\ J\ K^{-1}\ mol^{-1} =$ $\mathbf{+122.0\ J\ K^{-1}\ mol^{-1}}$
- $\Delta S^\circ = S^\circ_{products} - S^\circ_{reactants} = 2(192.77)\ J\ K^{-1}\ mol^{-1} - [191.56 + 3(130.7)]\ J\ K^{-1}\ mol^{-1} =$ $\mathbf{-198.1\ J\ K^{-1}\ mol^{-1}}$

Practice problem

Calculate $\Delta S^{\circ}_{universe}$ for the process of dissolving NaCl in water at 298 K.

Substance	ΔH°_{f} (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
NaCl (s)	–411.12	72.11
NaCl (aq)	–407.27	115.5

- NaCl (s) → NaCl (aq)
- $\boldsymbol{\Delta S^{\circ}{}_{universe} = -\frac{\Delta H^{\circ}{}_{sys}}{T} + \Delta S^{\circ}{}_{sys}}$
- $\Delta S^{\circ}_{sys} = 115.5\ J\ K^{-1}\ mol^{-1} - 72.11\ J\ K^{-1}\ mol^{-1} = +43.4\ J\ K^{-1}\ mol^{-1}$
- $\Delta H^{\circ}_{sys} = -407.27\ kJ\ mol^{-1} - (-411.12\ kJ\ mol^{-1}) = +3.85\ kJ\ mol^{-1}$
- $\Delta S^{\circ}{}_{universe} = -\frac{3850\ J\ mol^{-1}}{298\ K} + 43.4\ JK^{-1}mol^{-1} = \boldsymbol{+30.5\ JK^{-1}mol^{-1}}$

Practice problem

Calculate ΔG° for the formation of methane from carbon and hydrogen at 298 K using tabulated values of ΔH°_f and S°. Is the reaction product-favored or reactant-favored at equilibrium?

- $C\ (s) + 2\ H_2\ (g) \rightarrow CH_4\ (g)$

Substance	ΔH°_f (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
C (s)	0	5.6
H_2 (g)	0	130.7
CH_4 (g)	–74.87	186.26

- ΔH° = –74.87 kJ mol^{-1}
- ΔS° = 186.26 J K^{-1} mol^{-1} – [5.6 J K^{-1} mol^{-1} + 2(130.7 J K^{-1} mol^{-1})] =

-80.7 J K^{-1} mol^{-1}

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ = –74.87 kJ mol^{-1} – (298 K)(-0.0807 kJ K^{-1} mol^{-1}) = **–50.8 kJ mol^{-1}**
- **Product-favored**

Practice problem

Calculate ΔG° for the combustion of one mole of methane using ΔG°_f values of the products and reactants. Is the reaction product-favored or reactant-favored at equilibrium?

- $CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$

Substance	ΔG°_f (kJ mol^{-1})
CH_4 (g)	–50.8
O_2 (g)	0
CO_2 (g)	–394.359
H_2O (g)	–228.59

- ΔG° = –394.359 kJ mol^{-1} + 2(–228.59 kJ mol^{-1}) – (–50.8 kJ mol^{-1}) =

–800.7 kJ mol^{-1}

- **Product-favored**

Practice problem

The decomposition of liquid $Ni(CO)_4$ to produce Ni metal and CO has a ΔG° value of 40 kJ at 25 °C. Use values of ΔH° and S° for the reactants and products to estimate the temperature at which the reaction becomes product-favored at equilibrium.

- $Ni(CO)_4$ (l) → Ni (s) + 4 CO (g)

Substance	ΔH°_f (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Ni(CO)_4$ (l)	−632.0	320.1
Ni (s)	0	29.87
CO (g)	−110.525	197.674

- $\Delta H^\circ = 4(-110.525 \text{ kJ mol}^{-1}) - (-632.0 \text{ kJ mol}^{-1}) = +189.9 \text{ kJ mol}^{-1}$
- $\Delta S^\circ = 4(197.674 \text{ J K}^{-1} \text{ mol}^{-1}) + 29.87 \text{ J K}^{-1} \text{ mol}^{-1} - 320.1 \text{ J K}^{-1} \text{ mol}^{-1} = +500.5 \text{ J K}^{-1} \text{ mol}^{-1}$
- Entropically favored process (favored at high temperatures)
- The reaction becomes favorable at equilibrium once $\Delta G = \Delta H - T\Delta S \leq 0$
- $\Delta H \leq T\Delta S \rightarrow T \geq (189.9 \text{ kJ mol}^{-1})/(0.5005 \text{ kJ K}^{-1} \text{ mol}^{-1}) \rightarrow$ **$T \geq 379.4$ K**

Practice problem

Determine ΔG° for the formation of 1.00 mol of NH_3 (g) from nitrogen and hydrogen and use this value to calculate K for this reaction at 25 ˚C.

- N_2 (g) + 3 H_2 (g) → 2 NH_3 (g)
- For one mole of NH_3 (g), $\Delta G^\circ = -16.37$ kJ mol^{-1}
- $\Delta \mathrm{G} = -\mathrm{RTlnK} \rightarrow lnK = -\frac{-16370\ J\ mol^{-1}}{(8.314\ JK^{-1}mol^{-1})(298.15\ K)} \rightarrow \boldsymbol{K = 738}$

Practice problem

The value of K_{sp} for AgCl (s) at 25 ˚C is 1.8×10^{-10}. Determine ΔG˚ for the process Ag^{+} (aq) + Cl^{-} (aq) ⇔ AgCl (s) at 298.15 K.

- $K = K_{sp}^{-1} = 5.6 \times 10^{9}$
- $\Delta G^\circ = -RT\ln K = -(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})\ln(5.6 \times 10^{9}) = \mathbf{-55.62\ kJ\ mol^{-1}}$

Practice problem

Substance	ΔG°_f (kJ mol^{-1})
ICl (g)	–5.73
I_2 (g)	19.327
Cl_2 (g)	0

ICl (g) can be decomposed into I_2 (g) and Cl_2 (g).

2 ICl (g) → I_2 (g) + Cl_2 (g)

Calculate ΔG° for this reaction at 298 K using ΔG°_f values of the products and reactants. Is this reaction reactant-favored or product-favored at equilibrium?

- ΔG° = 19.327 kJ mol^{-1} – 2(–5.73 kJ mol^{-1}) = **+30.79 kJ**
- **Reactant-favored**

Practice problem

ICl (g) can be decomposed into I_2 (g) and Cl_2 (g).

2 ICl (g) → I_2 (g) + Cl_2 (g)

Calculate the value of ΔG at 298 K for this reaction if the reactant and products are mixed with the following partial pressures: 1.0 atm ICl, 1.0 x 10^{-3} atm I_2 and 1.0 x 10^{-3} atm Cl_2. Is the reaction spontaneous under these conditions?

- $Q = \frac{P_{I_2}P_{Cl_2}}{{P_{ICl}}^2} = \frac{(0.0010\ atm)(0.0010\ atm)}{(1.0\ atm)^2} = 1.0\times10^{-6}$
- $\Delta G = \Delta G^\circ + RT\ln Q = (30790\ J\ mol^{-1}) + (8.314\ J\ K^{-1}\ mol^{-1})(298\ K)\ln(1.0 \times 10^{-6})$ = **–3.44 kJ mol^{-1}**
- **Spontaneous**