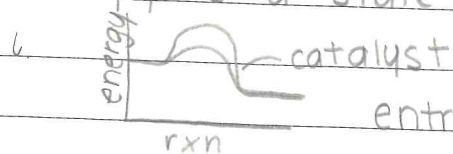


2 $S = k \ln W$ in which $k = 1.38 \cdot 10^{-23} \text{ J/K}$, $W = \#$ of microstates
Boltzmann's const.

3 Entropy is a state function



entropy is path independent

Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute 0 is zero

• All motion stops at absolute zero

• Only 1 arrangement

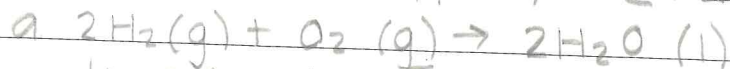
Standard molar entropy (J/molK): all positive at 298K

• Gas molar entropy generally greater than liquids and solids

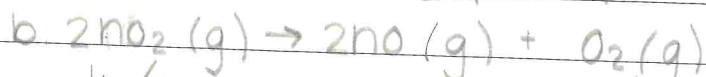
• molar entropy increases with molecular complexity

Calculations

$$\Delta S^\circ_{\text{system}} = \sum n \Delta S^\circ (\text{prod}) - \sum n \Delta S^\circ (\text{react})$$



$$\rightarrow 2(69.9) - [2(130.6) + 205.0] \text{ J/molK} = -327 \text{ J/K}$$



$$\rightarrow (2 \text{ mol NO}(\text{g}) \cdot 211 \text{ J/molK}) + (1 \text{ mol O}_2 \cdot 205 \text{ J/molK}) - (2 \text{ mol NO}_2(\text{g}) \cdot 240 \text{ J/molK}) = +147 \text{ J/K}$$

Predicting Entropy

Entropy increases with freedom of motion

$$S^\circ(\text{g}) > S^\circ(\text{l}) > S^\circ(\text{s})$$

Increasing volume, increase S°

More microstates

Increasing temperature, increase S°

Average kinetic energy increases, more microstates

4 Entropy increases with size and complexity

5 Entropy increases if:

• # of moles increases

• gas formation from liquids/solids

• liquid formation from solids

Temperature and Spontaneity

1 Some endothermic processes are spontaneous

2 Entropy can be calculated as the heat transferred reversibly to the system at temperature T

• $\Delta S = \frac{q_{\text{rev}}}{T}$ if heat gained, $\Delta S = -\frac{q_{\text{rev}}}{T}$ if heat lost

Zeroth Law of Thermodynamics

1 Two bodies in contact reach thermal equilibrium, with heat flowing from the warmer to cooler object

2 If the system and surroundings have a very small temperature difference, then heat will flow from the warmer to cooler reversibly

• At constant pressure, $\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{rxn}}}{T}$

• What is ΔS for an ice cube melting at 0°C ?

↳ $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$, 1.56 mol ice

$$\Delta S_{\text{sys}} = \frac{6.01 \text{ kJ}}{\text{mol}} \cdot 1.56 \text{ mol} = 34.3 \text{ kJ/K}$$

273K

• What is ΔS of the universe?

$\Delta S_{\text{surr}} = -34.3 \text{ kJ/mol}$, $\Delta S_{\text{univ}} = 0 \rightarrow \text{reversible}$

• What is ΔS for ice cube melting at 25°C ?

$\Delta S_{\text{sys}} = 34.3 \text{ kJ/mol}$ still!

$$\Delta S_{\text{surr}} = -\frac{6.01 \text{ kJ}}{\text{mol}} \cdot 1.56 \text{ mol} = -31.5 \text{ kJ/K}$$

298K

$$\Delta S_{\text{univ}} = 34.3 + (-31.5) = 2.8 \text{ kJ/K}$$