

CHM3400 Resources

Chapter 3: The Second Law of Thermodynamics FLORIDA INTERNATIONAL UNIVERSITY









The Second Law of Thermodynamics

- Entropy always increases!
- This may require us to include both the system and the surroundings.
- -In some cases, the entropy of the system decreases, which requires that the entropy of the surroundings increase.

$$H_2O_{(l)} \rightarrow H_2O_{(s)}$$

Entropy is Higher here

Entropy is Lower Here

This reaction is spontaneous because it is exothermic $(\Delta S_{system} + \Delta S_{surroundings}) > 0$

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Entropy Effects on Efficiency

- Imagine a heat source that is used to convert heat into work.
- •As heat is transferred, work is done. The conversion of heat into work does not affect the entropy of the system.
- •This transfer of heat however reduces the entropy of the heat source $(S = \frac{dq}{T})$.
- In order for there to be a net increase in entropy, a cold source is created. -AKA a cold sink.

$$\Delta S = -\frac{q}{T_{hot}} + \frac{q'}{T_{cold}}$$

•This means that not all of the energy of the heat source is converted into work.



Entropy Effects on Changing Volume

• Recall that if we allow a gas to expand isothermally, we can extract the maximum amount of work from the process. The internal energy of the system does not change, and therefore Q=W.

•This was expressed as:

$$W = -nRT \ln \frac{V_f}{V_i}$$

Using our equation for Entropy $(S = \frac{dq}{T})$, we can conclude that $S = \frac{dw}{T}$, therefore:

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

If the gas is expanding, $V_f > V_i$, and therefore $\Delta S > 0$ If the gas is compressed, $V_f < V_i$, and therefore $\Delta S < 0$

This can also be expressed in terms of a pressure change: $\Delta S = -nR \ln \frac{P_f}{P_f}$



Entropy Effects on Changing Temperature

 $S = \frac{dq}{T}$

Integrating results in $S = \frac{q}{T}$.

• Recall that a transfer of heat can be expressed as $q=C\Delta T$, or q=CdTTherefore:

$$S = \frac{C}{T} dT$$

Integrating therefore yields: $\Delta S = \int \frac{c}{\tau} dT$

$$\Delta S = C \ln \frac{T_f}{T_i}$$

 $\Delta S > 0$ when $T_f > T_i$

Entropy Effects on Phase Changes

• Recall that during a phase change, no work is done. All of the energy is transferred as heat. Therefore, $\Delta H = q$. Therefore: $\Delta S = \frac{\Delta H_T}{T}$

This is true for boiling, freezing, melting, etc.

Vaporization is endothermic, therefore $\Delta S > 0$

•Analogous relationships exist for other phase changes.

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Worked Example: Boiling Water

Calculate the entropy to heat water from 25 $^{\circ}\mathrm{C}$ to 100 $^{\circ}\mathrm{C}$

$$\Delta S = \frac{q}{T}$$
$$\Delta S = \frac{C}{T}$$
$$\Delta S = C \ln \frac{T_f}{T_i}$$
$$\Delta S = 75.29 \ln \frac{373 K}{298 K} kJ mol^{-1} K^{-1}$$
$$\Delta S = 0.0169 kJ mol^{-1} K^{-1}$$

Calculate the entropy of vaporization of water at 100 °C.

 $\Delta S = \frac{\Delta H_{vap}}{T}$ $\Delta S = \frac{40.7 \ kJ \ mol^{-1}}{373 \ K}$ $\Delta S = 0.11 \ kJ \ mol^{-1} K^{-1}$

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Worked Example: Boiling Water

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Entropy

• How many different ways can you arrange the marbles in a line such that:

- A) All 3 red marbles are together
- B) 2 red marbles together
- C) No red marbles together

 $S = k \ln \omega$

- S Entropy
- k Boltzmann Constant
- ω number of microstates (the number ways the particles in a thermodynamic system can be arranged).



Absolute Entropy

At T = 0 K, there is not thermal motion, and so there is no spatial disorder if the material is crystalline.

The conclusion therefore is that at 0 K all crystalline materials have the same entropy (0).

This is summarized by the Third Law of Thermodynamics

The entropies of all perfectly crystalline substances are the same at $\mathbf{T}=\mathbf{0}$ K.

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FIU Absolute Entropy

At low temperatures, the heat capacity of a substance is a function of temperature such that: $C(T) = aT^3$

Therefore, entropy at low temperature can be defined by:

$$S(T_f) - S(T_i) = \int \frac{C}{T} dT$$

$$S(T) - S(0) = \int \frac{aT^3}{T} dT$$

$$S(T) - 0 = a \int T^2 dT$$

$$S = \frac{1}{3}aT^3$$

$$S = \frac{1}{3}C(T)$$

FIU Absolute Entropy		
Substance	$S_{\rm m}^{\Theta}$ /(J K ⁻¹ mol ⁻¹)	
Gases		•Unsurprisingly molecules that are prope to a great
Ammonia, NH ₃	192.5	ensurprisingly, indice une prone to a great
Carbon dioxide, CO ₂	213.7	deal of disorder have higher absolute entropy values
Helium, He	126.2	deal of disorder have ingher absolute entropy values.
Hydrogen, H ₂	130.7	
Neon, Ne	146.3	
Nitrogen, N ₂	191.6	
Jxygen, O ₂	205.1	•Those that are highly ordered (crystalline) have much
water vapour, H ₂ O	188.8	i nose that are nighty ordered (crystanne) have much
Liquids		lower walnes
Benzene, C ₆ H ₆	173.3	lower values.
Ethanol, CH ₃ CH ₂ OH	160.7	
Nater, H ₂ O	69.9	
Solids		
Calcium oxide, CaO	39.8	
Calcium carbonate, CaCO ₃	92.9	
copper, Cu	33.2	
Diamond, C	2.4	
Graphite, C	5.7	
ead, Pb	64.8	
Magnesium carbonate, MgCO ₃	65.7	
lagnesium oxide, MgO	26.9	
odium chloride, NaCl	72.1	
ucrose, C ₁₂ H ₂₂ O ₁₁	360.2	
in, Sn (white)	51.6	
Sn (grey)	44.1	



Residual Entropy Worked Example

The entropy of $FClO_3$ at 0 K is approximately 12 kJ/mol. How many different states are possible?

 $S = k \ln \omega$ $S = R \ln \omega$ $\ln \omega = \frac{S}{R}$ $\omega = e^{\frac{S}{R}}$ $\frac{12\frac{kJ}{mol K}}{\frac{kJ}{mol K}}$ $\omega = 4.23$ $\omega = 4$



Total Entropy and Gibbs Energy

Recall that for a reaction to occur: $\Delta S_{total} > 0$

Recall

$$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys}$$

also that ΔS_{surr} can be expressed in terms of the enthalpy change of the
system:
$$\Delta S_{surr} = \frac{-\Delta H}{T}$$

$$\Delta S_{total} = \frac{-\Delta H}{T} + \Delta S_{sys}$$

$$T\Delta S_{total} = -\Delta H + T\Delta S_{sys}$$

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys}$$

$$\Delta G = \Delta H - T\Delta S_{sys}$$

Setting $-T\Delta S_{total} = \Delta G$
Where ΔG is the Change in
Gibbs Energy
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FIU Gibbs Energy

• By defining the total entropy change at a given temperature as the change in Gibbs Energy

$$-T\Delta S_{total} = \Delta G$$
• We can expect that a reaction may spontaneously proceed to maximize the total entropy change.
Total Entropy
Progress of
Change
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Gibbs Energy and Non-expansion Work

- The value for ΔG also provides a value for the maximum non-expansion work that can be extracted (at constant Temperature and Pressure).
- This includes any work other than that arising from expansion of the system.

-Electrical, mechanical, etc.

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$$\Delta G = w_{nonexp,max}$$

• This makes ΔG very powerful as it can be used to calculate the maximum non-expansion work that can be harnessed from a reaction.

$$\Delta H_{rxn} = \sum_{\text{products}} vH_m - \sum_{\text{reactants}} vH_m \qquad \Delta_r S^{\circ} = \sum_{\text{products}} vS_m^{\circ} - \sum_{\text{reactants}} vS_m^{\circ} \\ \Delta G_{rxn} = \sum_{\text{products}} v\Delta G_f - \sum_{\text{reactants}} v\Delta G_f \\ 22$$

• Summary the two probability of two probabi