

Physical Chemistry

Lecture 16

Third Law of Thermodynamics, and Reference States

Reference state

- ◆ Must tie the absolute values of state functions to some reference point
- ◆ One must define the constant, $S^\theta(0)$, in an equation like

$$S^\theta(T) = S^\theta(0) + \int_0^T \frac{C_p^\theta(T')}{T'} dT'$$

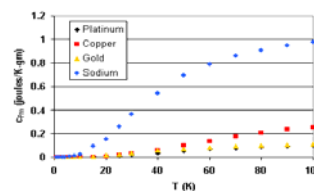
- ◆ Then the entropy at all other temperatures is found through this equation

Third law of thermodynamics

- ◆ Define the entropy at a specific set of conditions, namely $T = 0\text{ K}$
- ◆ **The entropy of all pure, crystalline substances is the same at the absolute zero of temperature. That entropy is assigned the value of zero.**
- ◆ Does not say that the entropy of every substance is zero at these conditions.

Heat capacity measurements

- ◆ Determine the heat capacity from 0 K to temperature of interest to be able to evaluate entropy
- ◆ Examples of heat capacity measurements



Debye theory of heat capacity of crystalline solids

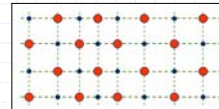
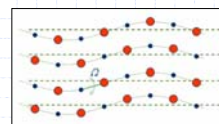
- ◆ Must know the heat capacity at all temperatures to define entropy
 - Difficult to measure for T near 0K
- ◆ Use a theoretical evaluation of low-temperature heat capacity by Peter J. W. Debye

$$C_p^\theta(T) = AT^3$$

- ◆ Debye considered the solid a group of vibrating atoms in a lattice

Debye model for heat capacity

- ◆ Lattice vibrations of a solid
 - Transverse
 - Longitudinal
- ◆ Each absorbs energy from an external source
- ◆ Sum over all possible lattice vibrations to obtain the manner in which energy is taken up
- ◆ Origin of heat capacity of solid materials



Methodology for using Debye theory to obtain standard entropy

- Evaluate integral in parts

$$S^\theta(T) = S^\theta(0) + \int_0^T \frac{C_p^\theta(T)}{T} dT + \int_{T'}^T \frac{C_p^\theta(T)}{T} dT$$

- Evaluation using Debye theory

$$S^\theta(T) = S^\theta(0) + \frac{C_p^\theta(T^*)}{3} + \int_{T'}^T \frac{C_p^\theta(T)}{T} dT$$

- The remaining integral is carried out numerically

Standard third-law entropies of selected elements at 298.15 K

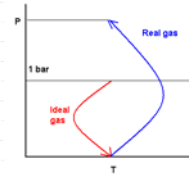
Element	S* (J/K-mole)	Element	S* (J/K-mole)
Aluminum	28.33	Nitrogen	191.61
Barium	62.80	Oxygen	205.13
Carbon (gr)	5.74	Silver	42.55
Chlorine	223.07	Sodium	51.21
Hydrogen	130.68	Sulfur (rh)	31.80
Iron	27.28	Tin	51.55
Mercury	76.02	Xenon	169.68

Reference state for real gases

- The standard state for any gas is the **equivalent ideal gas** at 1 bar
- This results in a "tricky" evaluation of entropy of the real gas
- The evaluation from the reference state requires one to integrate through a point which the real and ideal gas have in common

Reference state for real gases

- The entropy of a real gas is a sum of terms



$$\begin{aligned} S(T, P) &= S^\theta(T) + \Delta S \\ &= S^\theta(T) + \Delta S_{ideal} + \Delta S_{real} \end{aligned}$$

Reference state for real gases

- The entropy of a real gas is a sum of terms



$$\begin{aligned} S(T, P) &= S_m^\theta(T) - \int_p^0 \left(\frac{\partial V_m}{\partial T} \right)_{P, ideal} dP - \int_0^p \left(\frac{\partial V_m}{\partial T} \right)_{P, real} dP \\ &= S_m^\theta(T) - \int_p^0 \left(\frac{\partial V_m}{\partial T} \right)_{P, ideal} dP + \int_0^p \left(\frac{\partial V_m}{\partial T} \right)_{P, ideal} dP - \int_0^p \left(\frac{\partial V_m}{\partial T} \right)_{P, real} dP \\ &= S_m^\theta(T) - \int_p^0 \left(\frac{\partial V_m}{\partial T} \right)_{P, ideal} dP + \int_0^p \frac{R}{P} dP - \int_0^p \left(\frac{\partial V_m}{\partial T} \right)_{P, real} dP \\ &= S_{ideal}(T, P) + \int_0^p \left(\frac{R}{P} - \left(\frac{\partial V_m}{\partial T} \right)_{P, real} \right) dP \end{aligned}$$

Summary

- Reference values of state functions specified
- Third law of thermodynamics defines the entropy at a specific state
 - Pure crystalline material
 - 0 K
- Values at other states found by integration
- Debye's theory determines change at low T
- Reference state of gases is ideal gas at 1 bar
 - Integration through P = 0
 - "Correction" terms for nonideality