0.1 Semiconductor

Energy Gaps (eV):

• Conductor: 0

• Semiconductor $0 \le E_q \le 3.4$

• Insulator: ≥ 3.4

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• Opaque: ≤ 1.8

• Transparent: ≥ 3.1

• Coloured $1.8 < E_q < 3.4$

Note that when light is absorbed, we can see the complementary colour.

Intrinsic Semiconductors: Si This may occur due to the random formation of holes from electrons moving. For pure semiconductors, there are $2.2\times10^{12}e^-m^{-3}$

0.1.1 Extrinsic Semiconductors

If we dope the silicon with a group 15 element, we're adding more electrons. This adds a a donor state, a little bit below the conduction band.

In this case, we have a n-type semiconductor, with equation $\sigma = nq\mu_n$.

n is the number of electrons in the conduction band, q is the charge of a electron, and μ_n is the mobility of electrons.

If we dope it with a group 13 element, we're adding more holes. This forms a acceptor state slightly above the valence band.

This is a P-type semiconductor with equation $\sigma = pq\mu_p$.

p is the number of holes, μ_p is the mobility of positive charges, and q is the charge of electrons.

Usually, we add about $10^{20} \frac{dopants}{m^3}$, which is orders of magnitude higher than the amount from the intrinsic semiconductor. (either in holes or electrons).

$$\Delta E \propto (\frac{1}{n_l^2} - \frac{1}{n_h^2})$$

Gives the relative energy of energy levels.

Chapter 1

Tetrahedral APF

Via trigonometric manipulation (figure 1), by which we can determine the relationship between a (lattice parameter) and r (atomic radius) as $a=8r\times sin(35)$; By this,

$$\frac{V_{atoms}}{V_{cell}} = \frac{4\frac{4}{3} \times \pi r^3}{(8r \times sin(35))^3} = 0.34$$

Chapter 2

Thermodynamics

2.1 The Laws of Thermodynamics

1. For an isolated system

$$\Delta U = 0$$

For a closed system

$$\Delta U = q + W$$

q= heat in

W = work done on system

$$\Delta U = q - P\Delta V$$

can be rearranged to

$$q = \Delta H = \delta U + P\delta V$$

- . This is how we introduce enthalpy.
- 2. The Entropy of the Universe is always increasing

$$(\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0)$$

$$\Delta S_{System} - \frac{q}{T} > 0$$

$$T\Delta S_{System} - q > 0$$

$$T\Delta S_{system} - \Delta H > 0$$

But we're comfortable with energy decreasing, so we can multiply by -1 to get a quantity $\Delta G = \Delta H - T\Delta S$

3.

Things occur on their own (*spontaneously*) without the inpput of extra energy occur due to an increase in the entropy of the universe.

- G = Gibbs energy = $\Delta G = \Delta H T\Delta S$
- H = Enthalpy
- J = Joules
- \bullet K = Boltzmann
- M = Molarity
- N = number of moles
- \bullet P = pressure
- q = Heat transfer
- R = gas constant
- $S = \text{entropy} = \frac{q_{reversible}}{T}$
- T = temperature (thermodynamic, K)
- U = Internal energy
- V = Volume
- \bullet W = Work

There are three types of systems:

- 1. Open Both energy and matter can be exchanged through the system and environment.
- 2. Closed Only energy is exchangable
- 3. Isolated Neither energy nor matter can be exchanged.

In some special, useful cases (Constant P/1atm or Only expansion, PV work) gives $\Delta H = \Delta V + P\Delta V$.

An analogy for entropy - (q = sneezing) - In a crowded street, with high temperature vs. a quiet library (low temp)

At absolute zero, there is zero entropy. You can pick out a particle and know for sure that it's at the lowest energy. However, at infinite temperature, particles have equally distributed energies, and you'd have no idea what the energy of the particle is. Entropy then, is our level of certainty when blindly selecting a particle.

2.1.1 Internal Energy

We can have a lot of types of energy - translational/kinetic, rotational/angular, vibrational, electron translational, electronic spin, bond energy (eg. laser), nuclear ... etc

We don't really care or know all the energy sources, and thus we only consider changes in **Internal** Energy ΔU .

For entropy, since we know that at 0K we have S = 0, we can also define an absolute entropy.

As we often have processes occur with open atmosphere, we have constant P. The only work is "PV" work. This is given by

$$W = P\Delta V$$

A useful defined quantity of enthalpy accounts for work pushing back the atmosphere.

$$\Delta H = \Delta U + P\Delta V$$

Spontaneity: Types of Processes

 ΔH ΔS Spontaneity Example
- + all temperatures combustion of fuel
- - low temperatures freezing of water
+ + high temperatures melting of ice
+ - never n/a

We can actually create a plot of G = -TS + H of G against T. If we take a random point on the G axis, that is the G-intercept, or H.

We position the solid phase at the bottom of the g axis, the liquid phase above it, and the gas phase far above that $(\Delta H_{fusion} << \Delta H_{Vaporization})$ We know that entropy is always positive so we have a negative slope for the "solid" line, a steeper decreasing line for the liquid line and a very steep slope for the gas line. These lines all happen to intersect.

We know that for low Gibbs energies and low temperatures, we get a region that belongs to ice. Then, there's a small region where the liquid phase is stable, (273K to 373K) and then a region where the gas phase is stable. This graph is for 1 atm.

However at low (vapour) pressures, the intersections are different, and the vapour phase has a steeper slope than before, which can cause us to go from solid to gas without going through liquid.

Standard State is the state of an element at 298.15K and 1 bar.

2.1.3 State vs Path Function

A state function does not involve how a value was attained, only the current value at the point. A path function does. (Work , q(Heat))

2.1.4 Combustion of Octane

$$2C_8H_{18} + 25O_2 \rightarrow 16H_2O + 8O_2$$

 $\Delta H^C = 16\Delta H_F(H_2O) + 8\Delta H_FO_2 - (2\Delta H_FC8H_{18} + 25\Delta H_FO_2)$

$$\Delta_E H^C = -10160J$$

With given $\Delta H, \Delta S_{sys}$ is it Spontanteous?

per two mols of Octane.

PV work: Starting out with 25 mols of gas, we end up with 34 mols of gas, and we have gained 9 mols.

We can plug this into the ideal gas formula

$$P\Delta V = \Delta nRT$$
$$= 9(8.31)(298K)$$
$$= 22kJ.$$

2.1.5 Important Relationships

$$\Delta H_x = \Delta H_{f-Products} - \Delta H_{f-Reactants}$$

$$S_x = S_{Products} - S_{Reactants}$$

$$\Delta G_x = \Delta G_{f-Products} - \Delta G_{f-Reactants}$$

2.2 Intro to Phase Diagrams

If we draw a diagram of temperature against heat supplied, we can notice a few points:

- Plateaus at 0 and 100 degrees, where heat is being used for phase change. The enthalpy of Vaporization is 41 kJ/mol (a large plateau) vs the enthalpy of fusion at 0 degrees, which is only 6 kJ/mol
- The slopes are the specific heat capacity, given by $\frac{\Delta T}{q}$ or $q=\frac{1}{slope}\Delta T\frac{J}{molK}$

Then we get the heat flow equation: $q = n \times C_P \times \Delta T$ (molar, n = number of mols, C_P is molar heat capac at constant temp) or by mass, $q = mc\Delta T \frac{J}{gK}$. Equilibrium phase diagrams give the phase at equilibrium.

2.2.1 Phase Equilbrium

On a graph of P against T, we have regions of solid, liquid and gas. One of the unusual things about the H2O phase diagram is that the solid-liquid boundary has a negative slope (left).

We often keep pressure constant, P=1 atm, and variable temperature or chemistry/concentration/composition

For example, we can graph temperature against composition/percentage of carbon in iron-carbon steel.

2.2.2 Water-Sugar Phase Diagram

This is seen in sweetened drinks.

If we graph temperature against weight% or mass fraction sugar(pure water(0) to pure sugar (100)), we have an ice-liquid-gas boundary on the 0k-ice- 0-water- 100-gas -inf on the temperature axis at 0% sugar. At 12 weight percent sugar (12g sugar/100g liquid, 88 g water), we know it'll be liquid (technically syrup). However, if we go to 99% sugar, we'll get a saturated syrup, with liquid water and solid sugar at the point. That means, somewhere in between we have a saturation point, which will give a phase boundary. It's slanted (solubility/saturation limit) with a positive slope, as we can dissolve more sugar per unit of liquid.

Also, we have a downwards sloping line that intersects with this dissolution boundary, which suggests that at higher concentrations of sugar we stay liquid at lower temperatures. There's also a horizontal ultimate boundary where it'll be solid regardless of the concentration.

Adding salt to ice can really quickly cause it to melt and drop the temperature considerably (through endotherm).

You won't have to memorize the iron-carbon phase diagram;

Also

standard state (25C/1atm); standard enthalpy of formation ΔH_F^{θ} ; electrochemistry are not covered on the exam.

A computation:

Hydrogen gas is combusted and becomes water. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ at -10C. $\Delta H = ?$