The P-Chem Survival Guide:

NeighborhoodGeeks

Based on Elements of Physical Chemistry by Atkins

Chapter 1: Real and Ideal Gases

Key concepts:

* Equation of state
* Pressure, Volume, Temperature, amount of substance (n), ideal gas constant (R)
* Collision radius
* Mean free path
* Root mean square speed
* Effusion
* Gram’s law
* Ideal gas law
* Compression factor
* Van-Deer Waals Equation of State
* Virial Equation of State
* Collision frequency
* Maxwell Distribution of speeds
* Dalton’s Law of partial pressures
* Critical point
* Critical pressure, temperature, molar volume, etc.
* Vapour vs gas
* Joule-Thomson effect

Key Equations to Know:

Definitions:

Equation of state = when an equation can be utilized to model a substances behavior in a way that is a function of environmental variables (V, P, n, R, etc.)

Pressure = The amount of force exerted over a specified area

P = F/A = N/m^2 =

Collision radius = Van-Deer Waals radius of the molecule in question, usually assume hard-sphere, can be used to get volume occupied by molecule. Commonly denoted σ.

Mean free path = the average length between collisions denoted as λ

where k is the Boltzmann constant ()

Root mean square speed = the geometric average of molecular speed within a given volume.

Effusion = the rate at which a gas escapes through a single hole in a container of a fixed diameter.

Gram’s Law = relates the relative rates of effusion to molar masses of gases, the lighter the gas the faster the rate of effusion.

Ideal gas law = the workhorse of the gas laws, relates pressure and value to amount of substance, ideal gas constant, and temperature.

Compression Factor = The ratio of the ideal gases molar volume and that of the actual gas in question at a given temperature, commonly denoted Z.

Van-Deer Waals Equation of State = an equation of state that is accurate for real gases that accounts of the attractive and repulsive forces of the molecule (a) and the amount of space they take up (b).

Virial Equation of State = an equation of state the relates the compression factor to the molar volume which allows pressure to be written in terms of a power series with virial coefficients.

Collision frequency = commonly denoted as z, it is the average number of collisions a molecule makes within 1 second.

Maxwell Distribution of Speeds = a function that relates the pressure of a system with the speed of the molecules comprising the system.

Dalton’s Law of Partial Pressures = the total pressure of a system is comprised of the pressures exerted by each component of the gaseous mixture. Each gases partial pressure is a function of its mole fraction and the total pressure of the system.

Critical point = the point at which the critical constants of a substance are present.

Critical temperature = the temperature under which the application of pressure can transform a gas into a liquid.

Critical pressure = the pressure over which the application of it to a gas can transform it into a liquid.

Vapour = the gaseous phase of substance below its critical temperature (therefore this can occur through application of pressure alone)

Gas = the gaseous phase of a substance above its critical temperature (you cannot make this substance a liquid through pressure alone)

Joule-Thompson effect = the phenomenon that describes when a real gas is allowed to expand and temperature increases or decreases. The temperature increases when the gas has predominantly repulsive interactions, therefore this occurs when Z > 1. The temperature decreases when the gas has predominantly attractive interactions, therefore this occurs when Z < 1.

Chapter 2: The First Law of Thermodynamics

Key Concepts:

1. Work = Done to achieve motion against opposing force
2. Internal Energy = total energy of a substance including translation, kinetic, vibrational, and potential energy
3. Enthalpy = the heat at constant pressure
4. Heat = the flow of thermal energy
5. Heat capacity at constant pressure = the amount of heat required to increase the temperature of a substance by one degree C at constant pressure
6. Heat capacity at constant volume = the amount of heat required to increase the temperature of a bustance by one degree C at constant volume
7. Enthalpy of combustion = the heat released from a combustion reaction
8. Hess’ Law = Enthalpy of a unknown reaction can be broken down to enthalpies of known reactions.
9. State function = output of function depends only on the initial and final state, NOT on the path taken to achieve final state.
10. Enthalpy of ionization = the amount of heat released from removing one electron from a substance in the gaseous state at 1 bar.
11. Enthalpy of electron gain = the amount of heat gained from adding one electron to a substance in the gaseous state at 1 bar.
12. Enthalpy of formation = the amount of heat gained or lost from forming one mole of a substance from its elements at 1 bar.
13. Standard State = any phase of a substance at 1 bar.
14. Reference State = the most energetically favorable state of a substance at 1 bar.
15. Kirchhoff’s law = the change in enthalpy of a reaction occurring a non-standard conditions can be found by looking at the difference in heat capacities of the products and reactants of the reaction in question.
16. Bond Dissociation = the amount of energy required to break a bond
17. System = the objects of interest in a thermal event.
18. Surroundings = everything other than the body of interest in a thermal event, the system plus the surroundings equals the universe.
19. Open System = a system in which both heat and matter are allowed to be exchanged from the system to the surroundings and vice versa (think of a test tube that is left open to the atmosphere)
20. Isolated System = a system in which neither heat nor matter are allowed to be exchanged from the system to the surroundings or vice versa (think of a capped insulated container)
21. Closed System = a system in which only heat can be exchanged from the system to the surroundings (think a capped test tube).
22. Reversible process = a process in which an infinitely small changes in one property will allow the system to proceed in the reverse direction.
23. Adiabatic = a process in which the flow of heat is 0.
24. Diathermic = a process in which heat is allowed to flow
25. Phase transition = the process by which a substance changes from one state of matter to another
26. Melting/freezing = the process by which a substance changes from a solid to a liquid and vice versa
27. Condensation/vaporization = the process by which a substance changes from a gas to a liquid and vice versa
28. Sublimation/deposition = the process by which a substance changes from a solid to a gas and vice versa
29. Enthalpy of fusion = the heat absorbed by the system that allows a substance to transition from a solid to a liquid.
30. Enthalpy of vaporization = the heat absorbed by the system that allows a substance to transition from a liquid to a gas.
31. Bond enthalpy = the energy required to break a bond.
32. Equipartition Theorem = Theorem that states that the energy of a molecule will be equally distributed over the modes of motion such that each mode per quadratic contribution will increase the total energy by 1/2RT

Key Equations to know:

For a reversible process:

Chapter 3: The Second Law of Thermodynamics

Key Concepts:

1. Entropy = The amount of disorder or energy unavailable after the course of an event
2. Gibbs Free Energy = The amount of energy available to do nonexpansion work
3. Thermodynamic efficiency = The amount of work done per unit heat energy supplied
4. Trouton’s Rule = The entropy of vaporization is approximately 10.5R or 85 J/molK for nonassociated gases.
5. Absolute Entropy = The total amount of entropy a substance has
6. Weight = The number of ways to arrange a molecule in its lattice structure
7. Residual Entropy = The amount of entropy that persists at absolute zero for a nonperfect crystalline solid.
8. Nonexpansion work = Work that is done without a change in volume such as electrical work.

Key Equations to Know:

Chapter 4: Physical Transformations

Key Concepts:

1. Molar Gibbs Free Energy= the amount of free energy per mole of substance
2. VATVUS Diagram (Thermodynamic Square) = Pneumonic Device to get Gibbs equations
3. Gibbs Helmholtz Equation = States that the graph of G/T versus T has a slope of –H/T^2
4. Vapor Pressure = The amount of pressure the vapor phase of a substance exerts on the atmosphere
5. Clapeyron Equation = The equation relating the pressure to the change in entropy and volume of a thermodynamic transition
6. Clausius Clapeyron Equation = The equation relating the change in vapor pressure for a substance going from the liquid to the gas phase.
7. Phase Rule = Quickly gives degrees of freedom on a phase diagram
8. Degrees of Freedom = the number of variables (P, T, V) that can be changed such that the phase of the substance does not change.
9. Chemical Potential = The inherent susceptibility of a substance to chemical change per mole.
10. Partial Molar Quantities = The contribution of a particular component of a mixture to the total quantity of the mixture.
11. Mixing Gibbs Energy = The change in free energy by mixing chemical substances together.
12. Mixing Entropy = The change in entropy brought about by mixing chemical substances together.
13. Ideal Solutions = Solutions that obey Raoult’s Law for all concentrations of components
14. Raoult’s Law = States that the vapor pressure of a solution is related to the mole fraction of each component.
15. Henry’s Law = States that the vapor pressure of a solution is related to the henry constant and mole fraction of components, applies primarily to dilute solutions.
16. Ideal Dilute Solutions = solutions that follow Henry’s Law
17. Activities of Real Solutions = the effective molar concentration of components in a real solution that does not necessarily obey Raoult’s or Henry’s Law
18. Freezing point depression = The change in the observable freezing point of a substance caused by dissociated or associated particles in solution.
19. Boiling point elevation = The change in the observable boiling point of a substance caused by the dissociated or associated particles in solution.
20. Osmosis = The tendency of water to move from an area of low solute concentration to an area of high solute concentration.
21. Van’t Hoff Equation = The equation relating the osmotic pressure to the concentration of substances.
22. Nernst Distribution Law = when there are two immiscible liquids containing a solute, the ratio of the mole fraction of solute distributed in each layer is a constant.

Key Equations to know:

F is the degrees of freedom, C is the number of components, P is the number of phases present at the given temperature and pressure

Where p\* is the vapor pressure of the gas in its pure state, not in a mixture

Where capital pi is equal to the osmotic pressure

Chapter 5: Kinetics

Key Concepts:

Extent of reaction: How much the reaction “crack” is turned, can be either in the forward or reverse direction. The theoretical explanation behind limiting reagent and the basis of all kinetics measurements.

Steady-State Approximation: All reactive intermediates have equal rates of formation and destruction.

Transition state: The highest points on a reaction coordinate diagram, corresponds to the highest energy part of any reaction system.

Reaction rate: the rate at which the extent of reaction changes with time.

Collision theory: Reactions can only occur when two conditions are met, the molecules collide and that they collide with the rate energy and orientation to make an effective collision.

Transition State Theory: Reactions go to completion at a rate equal to the rate of a specific vibration to get the system over the “energy hump” of the activated complex.

Arrhenius Equation: Depicts the relationship between rate constants and temperature

Rate determining step: the step of the reaction mechanism that controls the rate of the reaction, the bottleneck in the process of going from reactants to products.

Half-life: the time it takes for 50% of a substance to react

Key Equations to know:

For first order kinetics:

For second order kinetics:

From Transition State Theory:

Chapter 6: Quantum Mechanics

Key Concepts:

Photoelectric effect: incident light on a metal must have a certain energy such that the energy of the photon can surpass the energy required to break the electron from the atoms in the material (work function value).

Debroglie wavelength: the wavelength of a particle is nothing both the ratio of planck’s constant and its linear momentum.

Particle on a circular wire: model of a particle such that it is confined to revolving around a center axis at a given radius, R, away from the axis. The potential energy of the particle is defined to be zero in this system, and its energy is solely the rotational energy of it as it rotates around its center axis. Useful for looking at aromatic compounds and their HOMO-LUMO wavelength transitions.

Particle in a 1-Dimensional Box: model of a particle such that it is confined to move along a line wherein its potential energy is defined as zero and its only energy is the linear kinetic energy of it moving along the 1-dimensional box, the potential energy is defined to be infinity outside the box. Useful for modeling highly conjugated systems such as 1,3,5 hexatriene or polyconjugated dyes. Limitation is that the length of the box needs to be slightly longer than the length of the bonds because the potential energy is not zero just outside the bond lengths.

Rigid Rotor: model of a particle rotating in space about a fixed axis.

Balmer Series: Series of spectral transitions for the hydrogen atom that were not able to be explained prior to the advent of quantum physics.

Quantum Harmonic Oscillator: Model of a particle vibrating such that it is basically like a mass-spring system. This is also called the quantum harmonic oscillator system because it behaves like a harmonic oscillator. Very useful for looking at vibrational modes of molecules and calculating their energies. Limitations are that this model assumes that the diatomic molecule behaves like a perfect harmonic oscillator and that it cannot dissociate after extensive pulling of the bonds. This is not true, thus diatomic molecules and other molecules to which this model is applied are anharmonic, and there are correction factors that ought to be used to correct for their anharmonicity.

Heisenberg Uncertainty Principle: The exact position and momentum of a particle cannot be known exactly, there are only certain tolerances that can be allows such that the product of the uncertainty in momentum and position is greater than or equal to ½ planck’s constant.

Key Equations to know: