

Chemistry BC3252y Course Outline

I. Properties of Gases and Equations of State

- A. Qualitative observations and definition of a gas
- B. Relations between p and V at constant temperature
 - 1. Boyle's law
 - 1. low pressures ($p < 1$ atm)
 - 2. wider range of pressures
 - 3. The virial equation: $pV_m = A + Bp^2 + Cp^3 + \dots$ for a given value of T .
 $B = B(T)$ = second virial coefficient
- C. Avogadro's law: A is a universal constant (independent of gas)
- D. Temperature
 - 1. Charles or Gay-Lussac's Law
 - 2. temperature scales and thermometers
 - 3. the absolute or Kelvin temperature scale: $T(K) = t(^{\circ}C) + 273.15$
 - 4. $V(p, T)$

$$\text{Expansivity } \alpha \text{ and compressibility } \beta: \alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \beta = -\frac{1}{V_0} \left(\frac{\partial V}{\partial P} \right)_T$$

note: sometimes defined with coefficient $(1/V)$ in place of $(1/V_0)$
application (to a liquid): alcohol in a thermometer

- 5. The gas constant R
- E. Ideal gas law (valid as p approaches zero): $pV_m = RT$
application: molecular weight determination

$$M = RT \lim_{p \rightarrow 0} \left(\frac{\rho}{p} \right) \quad \text{where } \rho = \text{density} = w/V$$

- F. Equations of State: $f(p, V_m, T) = 0$
 - 1. State variables: intensive and extensive
 - 2. Fluids: condensation and pV isotherms
 - 3. Critical phenomena
 - 4. Van der Waals' equation: $(p + n^2a/V^2)(V - nb) = nRT$
 - 5. Interpretation: attractive and repulsive forces between molecules

II. Thermodynamics: Basic Tools

- A. Fundamental definitions: Terms: *system, surroundings; isolated, closed, open*
- B. Forms of energy and units
- C. work: definition and some characteristics
 - 1. definition: $dw = -f dx$
 - 2. dw is an inexact differential:
work is a function of path, not a function of state
 - 3. "pV work" (work of expansion and compression): $dw = -p_{\text{ex}}dV$
 - a. expansion into a vacuum
 - b. against constant external pressure
 - c. Reversible isothermal expansion of an ideal gas: $w = -nRT \ln(V_2/V_1)$
 - 4. Heat q : also a function of path, not a state function.

D. Internal Energy U (sometimes E) and the First Law: $dU = dq + dw$

dU is an exact differential, U a state function

The zero of energy is arbitrary

Intensive and extensive properties

at constant volume $\Delta U = q_v$

E. Thermochemistry

1. Enthalpy: $H \equiv U + pV$

at constant pressure $\Delta H = q_p$

2. the relationship between ΔU and ΔH at constant temperature3. Hess' Law: using standard enthalpies (heats) of formation: $\Delta_f H^\circ$

4. Approximate bond energies

III. Applications of the First Law

A. Heat capacity:

1. definitions: $C_v \equiv \left(\frac{\partial U}{\partial T}\right)_v$ and $C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$

2. Relationship between the two heat capacities:

$$\text{In general: } C_p - C_v = \left[\left(\frac{\partial U}{\partial T}\right)_v + p \right] \left(\frac{\partial V}{\partial T}\right)_p$$

For an ideal monatomic gas: $C_p - C_v = nR$

3. Calorimetry

4. Adiabatic processes: for an adiabatic reversible expansion of an ideal gas

$(pV)^\gamma = \text{constant}$, where $\gamma = C_p/C_v$

5. Molecular interpretation of heat capacities

Degrees of freedom; equipartition of energy

Heat capacity of gases; of solids and liquids

B. Temperature dependence of ΔU and ΔH

1. Temperature dependence of heat capacities

Common representation: $C_{p,m} = a + bT + c/T^2$

2. $\Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$

ΔU and ΔH for reactions away from 25°C $\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT$

C. Pressure dependence of U and H for real gases

1. The Joule experiment. Result: $(\partial U/\partial V)_T = 0$

for an ideal gas U is function of T only, not V or p

2. $\Delta U(V, T)$ for real gases: $(\partial U/\partial V)_T \neq 0$ 3. $(\partial T/\partial p)_U > 0$ for real gases: molecular interpretation4. $\Delta H(p, T)$ for real gases: The Joule-Thompson experiment

Isenthalpic ($dH = 0$) conditions

The Joule-Thompson Coefficient: $\mu_{JT} = (\partial T/\partial p)_H$

Proof that $(\partial H/\partial p)_T = -\mu_{JT} C_p$

V. The Third Law and Temperature

A. The Third Law

1. Methods of refrigeration

Thermal equilibration with a cooler object

Joule-Thompson refrigeration

Boiling under reduced pressure

Adiabatic demagnetization

2. The third law:

At absolute zero, ΔS is zero for all reactions among pure, perfectly crystalline substances.

You cannot reach 0 K in a finite number of steps.

The entropy of any pure perfectly crystalline substance at 0 K is zero.

3. Third law entropies, S°

$$\text{Calculations: } S^\circ(T) = \int_{0\text{K}}^T \frac{C_p dT}{T} + \text{phase transition terms}$$

at very low T, the Debye law is used: $C = aT^3$

B. Statistical interpretation of entropy

1. Boltzmann's formula: $S = k \ln W$

3. Expansion of an ideal gas.

3. Residual entropy at 0 K. example: water

4. Entropy of mixing $\Delta_{\text{mix}}S = -nR(X_1 \ln X_1 + X_2 \ln X_2)$

C. Temperature and pressure dependence of the Gibbs free energy

1. Temperature dependence: the **Gibbs-Helmholtz equation**

$$\left(\frac{\partial(G/T)}{\partial T} \right)_p = -\frac{H}{T^2} \quad \text{or} \quad \left(\frac{\partial(G/T)}{\partial(1/T)} \right)_p = H$$

For chemical reactions (and similarly for phase transitions):

$$\left(\frac{\partial(\Delta_r G/T)}{\partial T} \right)_p = -\frac{\Delta_r H}{T^2} \quad \text{or} \quad \left(\frac{\partial(\Delta_r G/T)}{\partial(1/T)} \right)_p = \Delta_r H$$

2. Pressure dependence: $(\partial G/\partial p)_T = +V$, so $(\partial \Delta_r G/\partial p)_T = +\Delta_r V$

For an ideal gas, $G = G^\circ + nRT \ln(p/p^\circ)$ $p^\circ = p$ at standard pressure, 1 bar.

VI. Systems of Variable Composition

A. The chemical potential: $\mu_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i}$

direction of spontaneous change is towards lower μ_i

Fundamental equation for open systems (n's changing):

$$dG = -SdT + Vdp + \sum \mu_i dn_i$$

B. Partial molar quantities: for any extensive property Y

1. definition $Y_i = \left(\frac{\partial Y}{\partial n_i} \right)_{T,P,n'}$ where $n' =$ all n_j except n_i . Note that $G_k = \mu_k$

2. Additivity relations: e.g. $G = \sum_{i=1}^n n_i G_i = \sum_{i=1}^n n_i \mu_i$ [asserted, not proved.]

3. The Gibbs-Duhem equation

4. $d\mu_i = -S_i dT + V_i dp$ partial molar quantities S_i, V_i .

C. Mixtures of ideal gases

VII. Phase Equilibria

A. The **Gibbs phase rule** $f = 2 + c - p$

B. Single component systems

1. μ vs. T curves for phase changes at constant pressure: $d\mu = -S_m dT$

2. Single component phase diagrams

3. The **Clapeyron** equation: describes shape of coexistence curves

$$dp/dT = \Delta S/\Delta V = \Delta H/T\Delta V$$

4. The **Clausius-Clapeyron** equation: (final phase is gas; x = vap or sub)

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right) = -\frac{\Delta_x H}{R}$$

$$\text{integrate assuming constant } \Delta_x H \rightarrow \ln \left(\frac{p_2}{p_1} \right) = -\frac{\Delta_x H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

5. Effect of addition of inert gas

6. Multiple solid phases: examples sulfur and diamond

C. Two component systems

1. The Ideal solution

Raoult's Law: $p_{k,\ell} = X_{k,\ell} p_k^*$ for each component [$*$ = pure k]

$$\mu_{k,\ell}(T, p, X) = \mu_{k,\ell}^*(T, p) + RT \ln X_{j,\ell}$$

Thermodynamics of ideal solutions: $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$

2. Real solutions: activities

3. p-X and T-X phase diagrams

tielines, two phase regions

distillation

D. Other phase diagrams: azeotropes and eutectics

VII. Chemical equilibriaA. Stoichiometry and the extent of reaction ξ

If ν is the stoichiometric coefficient, then $dn_j = \nu_j d\xi$

(ν is – for reactants; + for products)

$$\Delta_r G \equiv (\partial G / \partial \xi)_{T,p}$$

$$\Delta_r G = \sum \nu_i \mu_i \quad \text{and} \quad dG = -SdT + Vdp + \Delta_r G d\xi$$

B. Equilibrium constants $\Delta G = \Delta G^\circ + RT \ln K_p$

for reactions among gases and pure condensed phases

C. Temperature dependence of the equilibrium constant

Van't Hoff equation (follows from the Gibbs-Helmholtz equation):

$$\left(\frac{\partial \ln K}{\partial (1/T)} \right)_p = - \frac{\Delta_r H^\circ}{R}$$

integrated form assuming constant $\Delta_r H^\circ$: $\ln \left(\frac{K_2}{K_1} \right) = - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

D. Effect of p and T on equilibria; comparison with LeChatelier's principleE. Using K 's to determine concentrations in equilibrium mixturesF. Equilibria in ideal solutions: K in terms of X_k or $[A]$

G. Non-ideal solutions

1. The principle of ionic strength
2. Activity replaces concentration: $\mu = \mu^\circ + RT \ln a_k$
3. Biochemical standard state ($pH = 7$ plus $\sum [H_n X] = 1$)

VIII. Chemical Kinetics

A. Phenomenological rate expressions

1. Order, molecularity, and the rate constant k

2. First order (1°) reactions:

$$-d[A]/dt = k [A] \quad \text{Integrated form: } \ln[A] = \ln [A]_0 - kt$$

$$\text{Half-life } t_{1/2} = (\ln 2)/k$$

3. Second order (2°) reactions: $-d[A]/dt = k[A]^2$ or $k[A][B]$ where $[A]_0 = [B]_0$

$$-d[A]/dt = k [A]^2 \quad \text{integrated form: } 1/[A] = 1/[A]_0 + kt$$

B. Experimental techniques

1. Method of initial rates: determining orders
2. Optical rotation: inversion of sucrose
3. Other physical observables: spectra, conductivity
4. Gas phase reactions with $\Delta n_{\text{gas}} \neq 0$: p_{tot} vs. time

C. Mechanisms

1. Pseudo-order reactions
2. Opposing reactions: $K_{\text{eq}} = k_f/k_b$
3. Rate limiting step
4. The steady state approximation
5. Catalysis
6. Enzyme kinetics: Michaelis-Menton mechanism:

$$\text{Rate} = d[\text{P}]/dt = v = k_2[\text{E}]_0[\text{S}]/(k_M + [\text{S}])$$

7. Chain reactions
8. Polymer kinetics

D. Temperature: the Arrhenius equation: $k(T) = A \exp(-E_a/RT)$

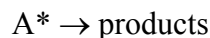
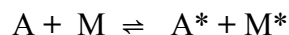
E. Theory of elementary reaction kinetics

1. Transition state theory: energy and entropy of activation

$$k_{\text{TST}} = (k_B T/h) \exp(\Delta S^\ddagger/R) \exp(\Delta H^\ddagger/RT)$$

Eyring plot: $\ln(k/T)$ vs. $(1/T)$ gives $\Delta S^\ddagger/R$ and $\Delta H^\ddagger/R$

2. Unimolecular reactions: The Lindemann-Hinshelwood mechanism



$$\text{rate law: } \frac{d[\text{products}]}{d(\text{time})} = \frac{k_1 k_2 [\text{A}][\text{M}]}{k_{-1} + k_2 [\text{M}]}$$

3. Bimolecular reactions: collisions and potential energy surfaces.

F. Modern experimental techniques

1. Relaxation methods
2. Beams and lasers: femtoseconds

G. Applications (Special Topics)

1. Oscillating reactions: non-linear dynamics
2. Kinetics and the stratosphere
 - a. Chapman reactions
 - b. Natural and anthropogenic ozone sinks