

Introduction to Chemical Thermodynamics

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(10 Lectures)

First Year
Michaelmas Term

Lecture Synopsis

1. *Introduction & Background.* Le Chatelier's Principle. Equations of state. Systems and their surroundings. Work and heat as currencies of energy.
2. *The First Law.* The conservation of energy: Internal energy. State functions and exact differentials. Expansion work. Reversible and irreversible changes. Heat capacity. Enthalpy.
3. *Thermochemistry.* The standard state. Standard enthalpy of a phase transition. Standard reaction enthalpy. Standard enthalpy of formation. Temperature dependence of reaction enthalpy.
4. *The Second Law.* The direction of spontaneous change: Entropy. The condition for equilibrium. Entropy of a phase transition. The variation of entropy with temperature and pressure. The third law. Statistical interpretation of entropy.
5. *Free Energy.* The direction of spontaneous change: Helmholtz and Gibbs free energies. Available work. Fundamental equations and Maxwell relations. Variation of Gibbs free energy with temperature and pressure.
6. *Phase Equilibria.* The condition for phase equilibrium. Clapeyron and Clausius-Clapeyron equations. One-component phase diagrams.
7. *Chemical Equilibria.* Variation of Gibbs free energy with composition: The chemical potential of a species in a mixture. The extent of reaction. The condition for chemical equilibrium. Gibbs free energy of formation. Gibbs free energy of reaction. The reaction quotient. The equilibrium constant and its temperature dependence.

Bibliography

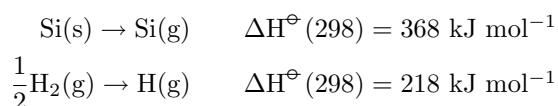
For a summary of the working equations of thermodynamics, and how they are derived, see the handout.
For a discussion of the concepts, see:

1. P. W. Atkins and J. de Paula, *Atkins Physical Chemistry* (7e, OUP, 2001); Chapters 1 to 9.
2. E. B. Smith, *Basic Chemical Thermodynamics* (4e, OUP, 1990); Chapters 1 to 8.

Problems

A. THE FIRST LAW

- A1. (a) Calculate the work done when 1 mole of an ideal gas (initial volume V_1) expands isothermally and reversibly to a final volume $V_2 = 3V_1$ at 298 K.
(b) Calculate the work done when 1 mole of an ideal gas (initial volume V_1) expands isothermally into an evacuated space to a final volume $V_2 = 3V_1$ at 298 K.
(c) The initial and final states of the gas are the same in parts (a) and (b), so the change in internal energy is the same in both cases. Reconcile your results for (a) and (b) with the First Law.
(d) One mole of $\text{CaCO}_3(\text{s})$ was heated in an open vessel at 1 atm pressure to 700 °C when it decomposed into $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$. Calculate the work done during the decomposition assuming that CO_2 may be regarded as an ideal gas.
- A2. A 0.825 g sample of benzoic acid was ignited in a bomb calorimeter in the presence of excess oxygen. The temperature of the calorimeter rose by 1.940 K from 298 K. In two separate experiments in the same apparatus, 0.498 g of fumaric acid and 0.509 g of maleic acid were ignited and gave temperature rises of 0.507 K and 0.528 K respectively. Calculate (a) the molar internal energy of combustion; (b) the molar enthalpy of combustion and (c) the molar enthalpy of formation of (i) fumaric acid and (ii) maleic acid. Comment on the difference between the enthalpies of formation of the two isomers. The standard enthalpy of formation of water is $-285.8 \text{ kJ mol}^{-1}$ and of CO_2 $-393.5 \text{ kJ mol}^{-1}$. The internal energy of combustion of benzoic acid is $-3251 \text{ kJ mol}^{-1}$. The relative molecular masses of benzoic, fumaric and maleic acids are 122, 116 and 116 respectively.
- A3. Calculate the average bond dissociation enthalpy of the Si–H bonds in SiH_4 from the following data. The molar enthalpy of combustion of $\text{SiH}_4(\text{g})$ to $\text{SiO}_2(\text{s})$ and $\text{H}_2\text{O}(\text{l})$ is $-1367 \text{ kJ mol}^{-1}$. The standard enthalpies of formation of SiO_2 and H_2O are -858 kJ mol^{-1} and -286 kJ mol^{-1} respectively. Also:



- A4. At 298 K, the standard enthalpy of formation ($\Delta_f H^\ominus$) of $\text{NH}_3(\text{g})$ is $-46.11 \text{ kJ mol}^{-1}$. Assuming that the molar heat capacities can be represented by expressions of the form $C_{p,m} = A + BT$, with the coefficients A and B given below, calculate $\Delta_f H^\ominus$ at 1000 K.

	N_2	H_2	NH_3
$A/\text{J K}^{-1} \text{ mol}^{-1}$	28.58	27.28	29.75
$10^3 B/\text{J K}^{-2} \text{ mol}^{-1}$	3.77	3.26	25.1

B. THE SECOND LAW

- B1. (a) At 25 °C the enthalpy change of the graphite \rightarrow diamond phase transition is 1.8961 kJ mol⁻¹ and the entropy change is -3.2552 J K⁻¹ mol⁻¹. Which is the spontaneous direction at 25 °C? Which direction is favoured by a rise in temperature?
- (b) Aragonite and calcite are two forms of crystalline CaCO₃. For the transition aragonite \rightarrow calcite, $\Delta G^\ominus(298) = -800 \text{ J mol}^{-1}$ and $\Delta V^\ominus(298) = 2.75 \text{ cm}^3 \text{ mol}^{-1}$. Assuming ΔV to be independent of pressure, at what pressure would aragonite become the stable form at 298 K?
- B2. Under suitable conditions the reaction $2\text{NO} + \text{N}_2\text{O}_4 \rightarrow 2\text{N}_2\text{O}_3$ can be studied in the gas phase. From the data below, calculate ΔG^\ominus for the reaction at (a) 298 K, and (b) 248 K. What implications do your results have for any attempts to produce and study N₂O₃?

	$\Delta_f H^\ominus(298)/\text{kJ mol}^{-1}$	$S^\ominus(298)/\text{J K}^{-1} \text{ mol}^{-1}$	$C_p/\text{J K}^{-1} \text{ mol}^{-1}$
NO	90.29	210.7	30.14
N ₂ O ₄	9.08	304.3	74.06
N ₂ O ₃	82.84	309.3	60.96

All components are to be treated as ideal gases; heat capacities may be taken as independent of temperature and are in fact average values over the required range.

- B3. The following table gives the molar heat capacity of lead over a range of temperatures. What is the standard molar Third Law entropy of lead at 25 °C?

T/K	10	15	20	25	30	50	70	100	150	200	250	298
$C_{p,m}/\text{J K}^{-1}\text{mol}^{-1}$	2.8	7.0	10.8	14.1	16.5	21.4	23.3	24.5	25.3	25.8	26.2	26.6

- B4. (a) How is entropy defined thermodynamically?
- (b) What role does ΔS play in determining the direction of spontaneous change?
- (c) On cold nights, water spontaneously freezes to form ice. How is this change consistent with your answer to (b)?
- (d) Given that $C_p(\text{H}_2\text{O}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_{\text{fus}} H^\ominus(\text{H}_2\text{O}) = 6.00 \text{ kJ mol}^{-1}$, calculate the change in entropy of a system comprising 1 mole of water at 10 °C that is cooled to 0 °C and then freezes to form ice at 0 °C.
- (e) Comment on the sign of ΔS you obtained in (d) in light of the microscopic changes occurring in the system.
- B5. (a) Calculate the entropy change of 3 moles of CH₄ that is heated from 298 K to 1098 K at a pressure of 1 atm, given that

$$C_p(\text{CH}_4)/\text{J K}^{-1} \text{ mol}^{-1} = 23.64 + 4.79 \times 10^{-2} T/\text{K} - 1.93 \times 10^{-5} (T/\text{K})^2$$

over the temperature range 298–2000 K.

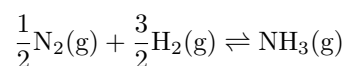
- (b) The entropy change of 2 moles of an ideal gas when it was expanded isothermally from V_A to V_B was found to be 5.595 J K⁻¹. Calculate the ratio V_B/V_A . If this isothermal expansion takes place

with the gas doing no work, what is the total entropy change of the system plus surroundings? Show that your result is consistent with the second law of thermodynamics.

C. PHASE AND CHEMICAL EQUILIBRIA

- C1. (a) The enthalpy of vaporization of water is 44.0 kJ mol^{-1} . Estimate the vapour pressure of water at $120 \text{ }^\circ\text{C}$.
 (b) Calculate the difference between the melting point of ice at 1 atm pressure and at the temperature of the triple point of water. The enthalpy of melting is 6.01 kJ mol^{-1} , the vapour pressure at the triple point is 4 Torr and the densities of ice and water at $0 \text{ }^\circ\text{C}$ are 0.917 g cm^{-3} and 1.0 g cm^{-3} respectively.

- C2. The standard Gibbs free energy of formation of $\text{NH}_3(\text{g})$ is $-16.49 \text{ kJ mol}^{-1}$ and the standard enthalpy of formation is $-46.11 \text{ kJ mol}^{-1}$. Assuming that $\Delta_f H^\ominus$ is independent of temperature, calculate the equilibrium constant, K_p , for the reaction



at (a) 298 K and (b) 1000 K. Then find (c) the temperature at which $K_p = 1$ and (d) the amounts of (i) N_2 , (ii) H_2 and (iii) NH_3 present when 1 mole of NH_3 is allowed to come to equilibrium at this temperature and 1 atm pressure.

- C3. The vapour pressures (in Torr) of solid and liquid chlorine are given by

$$p(s) = \exp(-3776/T + 24.32)$$

$$p(l) = \exp(-2669/T + 17.89)$$

where T is in Kelvin. Calculate (a) the temperature and (b) the pressure of the triple point of chlorine.

- C4. NO_2 is in equilibrium with its dimer at room temperature: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$. Use the following data for the pressures of NO_2 and N_2O_4 at equilibrium to calculate (a) the equilibrium constant for the reaction, and (b) the standard molar Gibbs free energy, (c) enthalpy and (d) entropy of dimerisation at 298 K.

	$p(\text{NO}_2)/\text{mmHg}$	$p(\text{N}_2\text{O}_4)/\text{mmHg}$
298 K	46	23
305 K	68	30

- C5. Between 400 K and 500 K, the standard free energy change for the gas phase reaction $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is given by

$$\Delta G^\ominus / \text{J mol}^{-1} = 83,680 - 14.52(T/\text{K})\ln(T/\text{K}) - 72.26(T/\text{K}).$$

Calculate (a) K_p , (b) ΔS^\ominus , and (c) ΔH^\ominus for the reaction at 450 K. Assuming all species to behave ideally, calculate also (d) the degree of dissociation of PCl_5 when 0.01 mol of PCl_5 is introduced into a 1 dm^3 vessel at 450 K.

D. FUNDAMENTAL EQUATIONS AND MAXWELL RELATIONS

The following problem comes from a past finals paper (GPC II/6/1993). It is more challenging than the above exercises, but if you are feeling confident you might like to give it a try.

D1. The reversible electric work required to polarize a gas of volume V by application of an electric field E is

$$\delta w_{\text{elec}} = VE dD$$

where D is the displacement polarization field.

(a) Using basic thermodynamic relations, show that

$$dU = TdS - p dV + VE dD$$

$$dA = -p dV - SdT + VE dD \quad (1)$$

where U and A are respectively the internal energy and Helmholtz free energy.

(b) The displacement and electric fields are related by $D = \epsilon E$, where the dielectric constant ϵ depends on the volume and temperature of the system. Express dD in terms of dV , dT and dE . Hence transform equation (1) into an expression for dA in terms of dV , dT and dE . Hence show that

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,E} + VE^2 \left(\frac{\partial \epsilon}{\partial T} \right)_V .$$

(c) Using the appropriate Maxwell relation, or otherwise, show that:

$$\left(\frac{\partial S}{\partial E} \right)_{V,T} = VE \left(\frac{\partial \epsilon}{\partial T} \right)_V .$$

(d) The dielectric constant of CH_3Cl gas is given approximately by

$$\epsilon = \epsilon_0 + \frac{N}{V} \frac{\mu^2}{3k_B T},$$

where ϵ_0 is the vacuum permittivity, N is the number of molecules, k_B is Boltzmann's constant, and $\mu = 6.24 \times 10^{-30}$ Cm is the permanent dipole moment of the molecule. Use the relation given in (c) above to evaluate the entropy change when one mole of CH_3Cl at constant volume and $T = 298$ K is subjected to an electric field $E = 10^9$ volt m^{-1} . Comment on your result.