

1st Year Physical Chemistry Tutorials

1.1 Thermodynamics I

Suggested texts:

Atkins, De Paula & Keeler, *Physical Chemistry*, 11th ed.
Smith, *Basic Chemical Thermodynamics*
Price, *Thermodynamics of Chemical Processes*, OUP Primer

Relevant lecture courses:

Chemical Thermodynamics – MT Year 1

You may want to cover the following points in your revision notes:

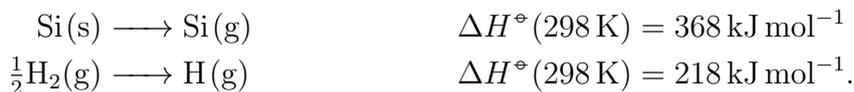
- a) **The 1st Law:** Heat, work & energy. Conservation of energy. State functions and exact differentials. Expansion work. Definitions and implications of adiabatic and isothermal changes. Reversible and irreversible changes. Enthalpy. Heat capacities (C_V , C_p). Intensive and extensive properties. The 0th Law.
- b) **Thermochemistry:** The standard state. Standard enthalpies (e.g. of phase transition, reaction, formation). Hess' Law and Hess cycles. Temperature dependence of reaction enthalpy (Kirchoff's Law), derivation from definition of C_p .
- c) **The 2nd Law:** Thermodynamic and statistical definitions of entropy. The Clausius inequality and the direction of spontaneous change. The variation of entropy with temperature and pressure. Entropy of phase transitions. Trouton's rule. The 3rd Law and absolute entropies. Residual entropy.
- d) **The Equipartition Theorem:** Deriving heat capacities (C_V , C_p) of ideal gases (Ar, CO₂, H₂O).

A. Discussion questions

1. What is meant by and what are the implications of: i) an isothermal change, ii) an adiabatic change, iii) a reversible change?
2. (a) Calculate the work done when one 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 one 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.
3. One mole of a perfect monatomic gas (with $C_V = \frac{3}{2}R$) is expanded adiabatically and reversibly to twice its initial volume, from an initial temperature of 298 K. Calculate (a) the final temperature of the gas and (b) the work done on the gas during the expansion.
4. Why is enthalpy more commonly used in chemistry than internal energy?
5. 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 (i) the molar internal energy of combustion, (ii) the molar enthalpy of combustion, and (iii) the molar enthalpy of formation of (a) fumaric acid and (b) 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 is $-393.5\text{ kJ mol}^{-1}$. The internal energy of combustion of benzoic acid is -3251 kJ mol^{-1} . The relative molecular masses of benzoic, fumaric and maleic acids are 122, 116 and 116 g mol^{-1} respectively.)

6. Calculate the average bond dissociation enthalpy of the Si–H bonds in SiH₄ from the following data.

The molar enthalpy of combustion of SiH₄ (g) to SiO₂ (s) and H₂O (l) is $-1367 \text{ kJ mol}^{-1}$. The standard enthalpies of formation of SiO₂ and H₂O are -858 kJ mol^{-1} and -286 kJ mol^{-1} respectively. Also:



7. (a) How is entropy defined i) thermodynamically, ii) statistically?
 (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 $\Delta_{\text{fus}}H^\circ(\text{H}_2\text{O}) = 6.00 \text{ kJ mol}^{-1}$, calculate the change in entropy of a system comprising 1 mol 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.
8. How do the enthalpy and entropy of a substance vary with temperature?
9. At 298 K, the standard enthalpy of formation ($\Delta_f H^\circ$) of NH₃(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 $\Delta_f H^\circ$ 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. Numerical problems

1. When 3.0 mol of O_2 is heated at a constant pressure of 3.25 atm its temperature increases from 260 K to 285 K. Given that the constant pressure molar heat capacity of O_2 is $29.4 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , ΔH and ΔU .
2. Calculate the standard enthalpy of formation of N_2O_5 at 298 K from the following data:



3. On arousal from hibernation a hamster can raise its body temperature by 30 K.
 - (a) Assuming that the heat required arises from the combustion of stearic acid ($C_{18}H_{36}O_2$), calculate the mass of stearic acid required by a 100 g hamster (neglecting heat losses).
 - (b) If the hamster continued to burn stearic acid at the rate of 0.1 g h^{-1} and its only heat loss mechanism were evaporation of water by sweating, calculate the rate at which it would need to sweat to maintain a constant temperature.

($\Delta_{\text{comb}}H(C_{18}H_{36}O_2) = -11.38 \times 10^3 \text{ kJ mol}^{-1}$, $\Delta_{\text{vap}}H(H_2O) = +44.0 \text{ kJ mol}^{-1}$, and the heat capacity of hamster tissue is $3.3 \text{ J K}^{-1} \text{ g}^{-1}$.)

4. The enthalpy of combustion of graphite at 25°C is $-393.51 \text{ kJ mol}^{-1}$ and that of diamond is $-395.41 \text{ kJ mol}^{-1}$. What is the enthalpy of the graphite \rightarrow diamond phase transition at this temperature?

The heat capacities at 25°C of graphite and diamond are $8.5 \text{ J K}^{-1} \text{ mol}^{-1}$ and $6.1 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Assuming that these values are independent of temperature, calculate the temperature at which the enthalpy of the graphite \rightarrow diamond phase transition is zero.

5. Calculate the molar entropy of a constant volume sample of $Ne(\text{g})$ at 500 K, given that it is 146.22 J K^{-1} at 298 K. Could one calculate the enthalpy of the sample at this temperature?

6. 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

7. Calculate the entropy change to the system associated with each of the following processes. Assume the gases behave ideally in each case.

- One mole of $\text{N}_2(\text{g})$ expands reversibly and isothermally to twice its volume.
- One mole of $\text{N}_2(\text{g})$ expands adiabatically to twice its volume.
- One mole of pure $\text{N}_2(\text{g})$ and one mole of pure $\text{O}_2(\text{g})$ are allowed to mix at constant total pressure.
- One mole of $\text{Ar}(\text{g})$ is heated at constant volume from 298 K to 308 K.
- One mole of $\text{Ar}(\text{g})$ is cooled at constant pressure from 110 K to 100 K.
- One mole of $\text{N}_2(\text{g})$ is liquefied reversibly at 77 K.

$$(\Delta_{\text{vap}}H(\text{N}_2) = 5.6 \text{ kJ mol}^{-1}.)$$

8. (a) Calculate the entropy change of three moles of CH_4 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.

- 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.

Solutions to numerical problems

A. Discussion questions

2. (a) $w = -2.72 \text{ kJ}$
(b) $w = 0 \text{ J}$
(d) $w = -8.09 \text{ kJ}$
3. (a) $T = 188 \text{ K}$
(b) $w = -1.38 \text{ kJ}$
5. (a) i. $\Delta_{\text{comb}}U = -1338 \text{ kJ mol}^{-1}$
ii. $\Delta_{\text{comb}}H = -1336 \text{ kJ mol}^{-1}$
iii. $\Delta_{\text{f}}H = -810 \text{ kJ mol}^{-1}$
(b) i. $\Delta_{\text{comb}}U = -1363 \text{ kJ mol}^{-1}$
ii. $\Delta_{\text{comb}}H = -1361 \text{ kJ mol}^{-1}$
iii. $\Delta_{\text{f}}H = -785 \text{ kJ mol}^{-1}$
6. $\Delta H = 326 \text{ kJ mol}^{-1}$
7. (d) $\Delta S = -24.7 \text{ J K}^{-1}$
9. $\Delta_{\text{f}}H^{\ominus} = -55.6 \text{ kJ mol}^{-1}$

B. Numerical problems

1. $q = 2205 \text{ J}$
 $\Delta H = 2205 \text{ J}$
 $\Delta U = 1581 \text{ J}$
2. $\Delta_{\text{f}}H^{\ominus} = +11.4 \text{ kJ mol}^{-1}$
3. (a) $m = 0.247 \text{ g}$
(b) $\text{rate} = 1.64 \text{ g h}^{-1}$
4. $\Delta_{\text{trs}}H = +1.9 \text{ kJ mol}^{-1}$
 $T = 1090 \text{ K}$
5. $S(500 \text{ K}) = 153 \text{ J K}^{-1}$
6. $S_{\text{m}}^{\ominus}(298 \text{ K}) \approx 65 \text{ J K}^{-1}$
7. (a) $\Delta S_{\text{sys}} = 5.76 \text{ J K}^{-1}$
(b) $\Delta S_{\text{sys}} = 0 \text{ J K}^{-1}$
(c) $\Delta S_{\text{sys}} = 11.5 \text{ J K}^{-1}$
(d) $\Delta S_{\text{sys}} = 0.412 \text{ J K}^{-1}$
(e) $\Delta S_{\text{sys}} = -1.98 \text{ J K}^{-1}$
(f) $\Delta S_{\text{sys}} = -72.7 \text{ J K}^{-1}$
8. (a) $\Delta S = 175 \text{ J K}^{-1}$
(b) $V_{\text{B}}/V_{\text{A}} = 1.4$