

CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

- . Physical Chemistry, [Robert J. Silbey](#), Robert A. Alberty, [Moungi G. Bawendi](#)
- . Physical Chemistry, Ira N. Levine

THERMOCHEMISTRY

State Functions and Exact Differentials

State function: A property of the state depends on only on the current state of a system and is independent of its history: H, U...

Path function: Physical quantities with values depend on the path between two states: w, q (a property of the path)

$\Delta U = \int_i^f dU$, ΔU : depends initial and final states (independent of the path)

dU : Exact differential, an exact differential is an infinitesimal (infinitely small) quantity.

$$q = \int_{i,path}^{f,path} dq$$

THERMOCHEMISTRY

Changes in Internal Energy

$$U = f(V, T)$$

Internal energy change

$$dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT \quad \text{General expression for a change in } U \text{ with } T \text{ and } V.$$

π_T : internal pressure $\pi_T = 0$ for perfect gas

Changes in internal energy of constant pressure

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_v$$

THERMOCHEMISTRY

Changes in Internal Energy

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \text{ Expansion coefficient ; } \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \text{ isothermal compressibility}$$

$$\left(\frac{\partial U}{\partial T} \right)_p = \alpha \pi_T V + C_v \quad \pi_T = 0 \text{ for perfect gas}$$

$$\left(\frac{\partial U}{\partial T} \right)_p = C_v ; \quad C_p - C_v = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_p$$

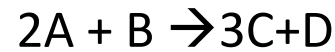
$$H = U + PV = U + nRT$$

$$C_p - C_v = \left(\frac{\partial(U+nRT)}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_p = nR$$

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa_T} \text{ this equation reduces to equation above for a perfect gas when } \alpha = 1/T \text{ and } \kappa_T = 1/p$$

THERMOCHEMISTRY

Standard reaction enthalpy;



$$\Delta_r H^\theta = \{3H_m^\theta(C) + H_m^\theta(D)\} - \{2H_m^\theta(A) + H_m^\theta(B)\}$$

$$\Delta H_r^\ominus = \Delta_r H^\theta = \sum_{products} \nu H_m^\theta - \sum_{reactants} \nu H_m^\theta \quad \text{standard reaction enthalpy}$$

Hess's Law:

Standard reaction enthalpies can be combined to obtain the value for another reaction. This application of the First Law is called Hess's Law.

The standard reaction enthalpy is the sum of the values for the individual reaction into which the overall reaction may be divided.

THERMOCHEMISTRY

Standard enthalpies of formation

$$\Delta H_f^\ominus, \Delta_f H^\ominus \quad \Delta_f H^\ominus = 0 \text{ for elements,}$$

For any reaction

$$\Delta H_f^\ominus = \Delta_f H^\theta = \sum_{\text{products}} \nu H_f^\theta - \sum_{\text{reactants}} \nu H_f^\theta \quad (\text{practical implementation})$$

THERMOCHEMISTRY

The temperature dependence of reaction enthalpies:

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Enthalpy changes from T_1 to T_2 ,

The standard reaction enthalpy changes from

$$\Delta H_r^\ominus(T_2) = \Delta H_r^\ominus(T_1) + \int_{T_1}^{T_2} \Delta C_p^\ominus dT \quad \text{Kirchhoff's Law}$$

$$\Delta H_r^\ominus(T_2) = \Delta H_r^\ominus(T_1) + \Delta C_{p,r}^\ominus(T_2 - T_1)$$

$$\Delta C_{p,r}^\ominus = \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus$$