

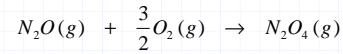
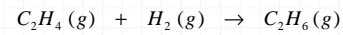
## Physical Chemistry

### Lecture 25

Hess's Rule, Temperature Dependence of Enthalpy of Reaction, and Adiabatic Flame Temperature Calculations

## Thermodynamics of reaction processes

- Often faced with the need to calculate the change of a thermodynamic variable in a reaction that may not be tabulated

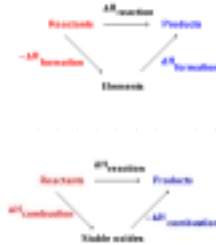


- Applies to all thermodynamic variable

$$\Delta H_{reaction} \quad \Delta S_{reaction} \quad \Delta U_{reaction} \quad \Delta A_{reaction} \quad \Delta G_{reaction}$$

## Cyclic properties of thermodynamic functions

- Consider a cycle involving reaction
- Change in a thermodynamic variable
  - Change through a cycle is zero
  - Change along one path between two states must equal that along another connecting the two states
- True for  $\Delta H$ ,  $\Delta U$ ,  $\Delta S$ ,  $\Delta A$ ,  $\Delta G$



## Hess's rule

- The cyclic property involving reaction is codified in Hess's rule

$$\Delta H_{reaction} = \sum_k v_k \Delta_f H_{k,m}$$

- True of any state function

$$\Delta U_{reaction} = \sum_k v_k \Delta_f U_{k,m}$$

$$\Delta S_{reaction} = \sum_k v_k \Delta_f S_{k,m}$$

$$\Delta A_{reaction} = \sum_k v_k \Delta_f A_{k,m}$$

$$\Delta G_{reaction} = \sum_k v_k \Delta_f G_{k,m}$$

## Hess's rule and combustions

- The cyclic property is also true when the intermediate state is the stable oxides

$$\Delta H_{reaction} = -\sum_k v_k \Delta H_{k,m,combustion}$$

$$\Delta U_{reaction} = -\sum_k v_k \Delta U_{k,m,combustion}$$

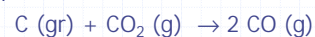
$$\Delta S_{reaction} = -\sum_k v_k \Delta S_{k,m,combustion}$$

$$\Delta A_{reaction} = -\sum_k v_k \Delta A_{k,m,combustion}$$

$$\Delta G_{reaction} = -\sum_k v_k \Delta G_{k,m,combustion}$$

## Example: Boudouard's reaction

- Reaction



- By Hess's rule

$$\Delta H_{reaction}^\theta(298.15\text{K}) = 2\Delta_f H_m^\theta(CO) - \Delta_f H_m^\theta(C) - \Delta_f H_m^\theta(CO_2)$$

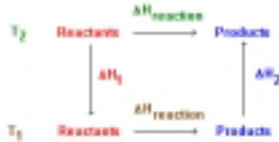
- From Table 6.1, one can find the enthalpies of formation

$$\Delta H_{reaction}^\theta(298.15\text{K}) = 2(-110.525\text{kJ}) - (0\text{kJ}) - (-393.509\text{kJ}) = 172.459\text{kJ}$$

- Enthalpies and energies of formation of elements are zero, by definition

## Temperature dependence of thermodynamic quantities

- Chemical reactions are often carried out at temperatures other than those for which information is tabulated
- Use cyclic properties to determine changes in thermodynamic properties at other temperatures



## Temperature dependence of enthalpy of reaction

- Enthalpy change is independent of the path

$$\Delta H_{\text{reaction}}(T_2) = \Delta H_1 + \Delta H_{\text{reaction}}(T_1) + \Delta H_2$$

- The two steps are simply heating of materials

$$\begin{aligned} \Delta H_{\text{reaction}}(T_2) &= \int_{T_1}^{T_2} C_{p,\text{reactants}}(T) dT + \Delta H_{\text{reaction}}(T_1) + \int_{T_1}^{T_2} C_{p,\text{products}}(T) dT \\ &= \Delta H_{\text{reaction}}(T_1) + \int_{T_1}^{T_2} \Delta C_p(T) dT \end{aligned}$$

- Evaluation of the heat-capacity difference allows estimate of enthalpy change at different temperature

## Temperature dependence of thermodynamic quantities

- Determining temperature dependence involves evaluation of change for both reactants and products

$$\Delta H_{\text{reaction}}^{\theta}(T_2) = \Delta H_{\text{reaction}}^{\theta}(T_1) + \int_{T_1}^{T_2} \Delta C_p^{\theta}(T) dT$$

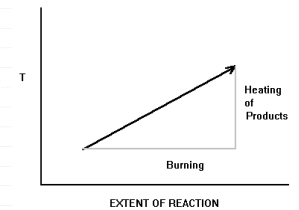
$$\Delta U_{\text{reaction}}^{\theta}(T_2) = \Delta U_{\text{reaction}}^{\theta}(T_1) + \int_{T_1}^{T_2} \Delta C_v^{\theta}(T) dT$$

$$\Delta S_{\text{reaction}}^{\theta}(T_2) = \Delta S_{\text{reaction}}^{\theta}(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_p^{\theta}(T)}{T} dT$$

## Adiabatic flame temperature

- Question: What is the temperature in a flame?
- Can answer this question in a limit
  - Heat generated raises temperature of the products
  - No losses of heat – adiabatic process

- Solve for  $T_2$ , **adiabatic flame temperature**
  - Can be difficult because it may be a complex equation in  $T_2$
  - Must know what materials are "products"



$$\int_{T_1}^{T_2} C_{p,\text{products}}^{\theta}(T) dT = -\Delta H_{\text{combustion}}^{\theta}(T_1)$$

## Adiabatic flame temperatures

Fuel	Oxidizer	Reaction	$T_{ad}$ (K)
Hydrogen	Oxygen	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	3100
Methane	Oxygen	$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	3000
Methane	Air	$\text{CH}_4 + 2 \text{O}_2 + 8 \text{N}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 8 \text{N}_2$	2200
Octane	Oxygen	$\text{C}_8\text{H}_{18} + 25/2 \text{O}_2 \rightarrow 8 \text{CO}_2 + 9 \text{H}_2\text{O}$	3100
Acetylene	Oxygen	$\text{C}_2\text{H}_2 + 5 \text{O}_2 \rightarrow 4 \text{CO}_2 + 2 \text{H}_2\text{O}$	3300
Cyanogen	Oxygen	$\text{C}_2\text{N}_2 + 5 \text{O}_2 \rightarrow 2 \text{CO}_2 + \text{N}_2$	4800
Producer gas	Air	$2 \text{CO} + 4 \text{H}_2 + 3 \text{O}_2 + 12 \text{N}_2 \rightarrow 2 \text{CO}_2 + 4 \text{H}_2\text{O} + 12 \text{N}_2$	2400
Methylhydrazine	Nitrogen tetroxide	$\text{CH}_3\text{NH}_2 + \text{N}_2\text{O}_4 \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2 + 2 \text{N}_2$	3000

## Summary

- Hess's rule allows estimation of thermodynamic changes for a wide variety of chemical reactions
- Use of thermodynamic cycles allows estimation of thermodynamic changes at conditions other than those in tables, particularly at other temperatures
- Adiabatic flame temperature calculation relies on a similar cyclic calculation