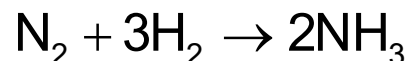


CH365 Chemical Engineering Thermodynamics

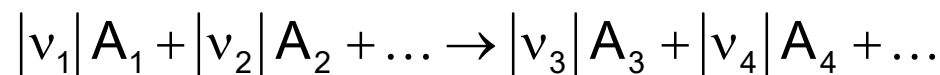
Lesson 18

Temperature Dependence of ΔH°

Chemical Reactions



$$v_{\text{N}_2} = -1 \quad v_{\text{H}_2} = -3 \quad v_{\text{NH}_3} = +2$$



A_i = chemical formula

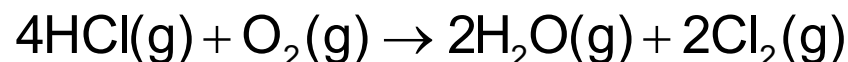
$|v_i|$ = stoichiometric coefficient

positive (+) for products

negative (-) for reactants

$$\Delta H^\circ = \sum_i v_i H_i^\circ \quad \text{Eq. 4.15}$$

$$\Delta H^\circ = \sum_i v_i H_{f,i}^\circ \quad \text{Eq. 4.16}$$



$$\Delta H^\circ = \sum_i v_i H_{f,i}^\circ = 2\Delta H_{f,\text{H}_2\text{O}}^\circ - 4\Delta H_{f,\text{HCl}}^\circ$$

$$\Delta H_{298}^\circ = (2)(-241,818) - (4)(-92307) = -114,408 \text{ J}$$

BLUF: Need T
instead of T_{ref}

Standard Reactions

$$dH_i^o = C_{p_i}^o dT \quad \text{Eq. 2.20}$$

Standard reactions are
always at $P = 1$ bar

multiply by v_i and sum over all i :

$$\sum_i v_i dH_i^o = \sum_i v_i C_{p_i}^o dT$$

$$\sum_i d(v_i H_i^o) = \sum_i v_i C_{p_i}^o dT$$

$$d\left(\sum_i (v_i H_i^o)\right) = \sum_i v_i C_{p_i}^o dT \quad \Delta H^o = \sum_i v_i H_i^o \quad \text{Eq. 4.15}$$

$$d\Delta H^o = \sum_i v_i C_{p_i}^o dT \quad \Delta C_P^o \equiv \sum_i v_i C_{P_i}^o \quad \text{Eq. 4.17}$$

$$d\Delta H^o = \Delta C_P^o dT \quad \text{Eq. 4.18}$$

$$\Delta H^o = \Delta H_0^o + R \int_{T_0}^T \frac{\Delta C_P^o}{R} dT \quad \text{Eq. 4.19}$$

Next step: derive
convenient integrated
forms for integral
(IDCPH, MDCPH)

Integrated Forms

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A \cdot (T - T_0) + \frac{\Delta B}{2} \cdot (T^2 - T_0^2) + \frac{\Delta C}{3} \cdot (T^3 - T_0^3) + \Delta D \cdot \left(\frac{T - T_0}{T \cdot T_0} \right) \quad \text{Eq. 4.20}$$

$$\Delta A = \sum_i v_i \cdot A_i, \text{ etc.}$$

$$\frac{\langle \Delta C_p^\circ \rangle_H}{R} = \Delta A + \frac{\Delta B}{2} \cdot (T + T_0) + \frac{\Delta C}{3} \cdot (T^2 + T_0^2 + T \cdot T_0) + \frac{\Delta D}{T \cdot T_0} \quad \text{Eq. 4.21}$$

$$\Delta H^\circ = \Delta H_0^\circ + \langle \Delta C_p^\circ \rangle_H (T - T_0) \quad (T - T_0) \text{ factored out}$$

Eq. 4.22

Derived on
next slide

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \text{IDCPH}$$

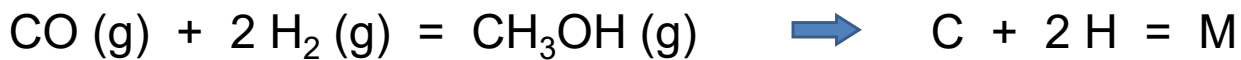
Looks like ICPH and MCPH from
lesson 16 (slide 4)

In book: IDCPH(T_0, T, DA, DB, DC, DD)

$$\frac{\langle \Delta C_p^\circ \rangle_H}{R} = \text{MDCPH}$$

In book: MDCPH(T_0, T, DA, DB, DC, DD)

Derivation of Integrated Forms at T Slide 9



Important derivation
(not in book)

$$v_{\text{CO}} = -1 = v_{\text{C}} \quad v_{\text{H}_2} = -2 = v_{\text{H}} \quad v_{\text{CH}_3\text{OH}} = +1 = v_{\text{M}}$$

Bring reactants from T to T_0 , react at T_0 , then bring products from T_0 to T

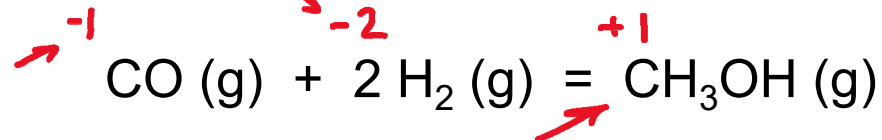
Method: write Cp integrals for each species, add standard heat, reverse order of integration on reactants, replace coefficients with v's, and group integrals together:

$$\begin{aligned} \Delta H &= \underbrace{R \int_T^{T_0} \frac{C_P^{\text{C}}}{R} dT + R \int_T^{T_0} 2 \frac{C_P^{\text{H}}}{R} dT}_{\text{cool the reactants}} + \underbrace{\Delta H_{\text{R}}^{\circ}}_{\text{react}} + \underbrace{R \int_{T_0}^T \frac{C_P^{\text{M}}}{R} dT}_{\text{warm the products}} \\ &= R \int_{T_0}^T \left\{ v_{\text{C}} \frac{C_P^{\text{C}}}{R} + v_{\text{H}} \frac{C_P^{\text{H}}}{R} + v_{\text{M}} \frac{C_P^{\text{M}}}{R} \right\} dT + \Delta H_{\text{R}}^{\circ} \\ &= R \int_{T_0}^T \left\{ v_{\text{C}} (A_{\text{C}} + B_{\text{C}}T + C_{\text{C}}T^2 + D_{\text{C}}T^{-2}) + v_{\text{H}} (A_{\text{H}} + B_{\text{H}}T + C_{\text{H}}T^2 + D_{\text{H}}T^{-2}) + v_{\text{M}} (A_{\text{M}} + B_{\text{M}}T + C_{\text{M}}T^2 + D_{\text{M}}T^{-2}) \right\} dT + \Delta H_{\text{R}}^{\circ} \\ &= R \int_{T_0}^T \left\{ v_{\text{C}}A_{\text{C}} + v_{\text{C}}B_{\text{C}}T + v_{\text{C}}C_{\text{C}}T^2 + v_{\text{C}}D_{\text{C}}T^{-2} + v_{\text{H}}A_{\text{H}} + v_{\text{H}}B_{\text{H}}T + v_{\text{H}}C_{\text{H}}T^2 + v_{\text{H}}D_{\text{H}}T^{-2} + v_{\text{M}}A_{\text{M}} + v_{\text{M}}B_{\text{M}}T + v_{\text{M}}C_{\text{M}}T^2 + v_{\text{M}}D_{\text{M}}T^{-2} \right\} dT + \Delta H_{\text{R}}^{\circ} \\ &= R \int_{T_0}^T \left\{ \underbrace{v_{\text{C}}A_{\text{C}} + v_{\text{H}}A_{\text{H}} + v_{\text{M}}A_{\text{M}}}_{\Delta A} + v_{\text{C}}B_{\text{C}}T + v_{\text{H}}B_{\text{H}}T + v_{\text{M}}B_{\text{M}}T + v_{\text{C}}C_{\text{C}}T^2 + v_{\text{M}}C_{\text{M}}T^2 + v_{\text{H}}C_{\text{H}}T^2 + v_{\text{C}}D_{\text{C}}T^{-2} + v_{\text{H}}D_{\text{H}}T^{-2} + v_{\text{M}}D_{\text{M}}T^{-2} \right\} dT + \Delta H_{\text{R}}^{\circ} \\ &\quad \Delta A = v_{\text{C}}A_{\text{C}} + v_{\text{H}}A_{\text{H}} + v_{\text{M}}A_{\text{M}}, \quad \Delta B = v_{\text{C}}B_{\text{C}} + v_{\text{H}}B_{\text{H}} + v_{\text{M}}B_{\text{M}}, \quad \text{etc.} \\ &= R \int_{T_0}^T \left\{ \Delta A + \Delta B \cdot T + \Delta C \cdot T^2 + \Delta D \cdot T^{-2} \right\} dT + \Delta H_{\text{R}}^{\circ} \\ &= R \int_{T_0}^T \frac{\Delta C_P}{R} dT + \Delta H_{\text{R}}^{\circ} = R \cdot \text{IDCPH} + \Delta H_{\text{R}}^{\circ} \end{aligned}$$

(BLUF: This derivation shows that this equation for calculating ΔH only works when T is the same for reactants and products.)

Example 4.6

Calculate the standard heat of formation of the methanol synthesis reaction at 800 °C.



$$\Delta H_{298}^{\circ} = \sum_i v_i H_{f,i}^{\circ} = (1) \cdot (-200,660) + (-1) \cdot (-110,525) = -90,135 \text{ J}$$

Eq. 4.16

| i | v_i | A ✓ | Bx10 ³ ✓ | Cx10 ⁶ ✓ | Dx10 ⁻⁵ ✓ |
|--------------------|-------|-------|---------------------|---------------------|----------------------|
| CH ₃ OH | 1 | 2.211 | 12.216 | -3.450 | 0.000 |
| CO | -1 | 3.376 | 0.557 | 0.000 | -0.031 |
| H ₂ | -2 | 3.249 | 0.422 | 0.000 | 0.083 |

✓ look-ups

Table C.1
page 656

$$\Delta A = (1) \cdot (2.211) + (-1) \cdot (3.376) + (-2) \cdot (3.249) = -7.663$$

$$T = 800 \text{ °C} = 1073 \text{ K}$$

$$\Delta B = (1) \cdot (12.216) + (-1) \cdot (0.557) + (-2) \cdot (0.422) = 10.815 \times 10^{-3}$$

$$T_0 = 25 \text{ °C} = 298 \text{ K}$$

$$\Delta C = (1) \cdot (-3.450) + (-1) \cdot (0.000) + (-2) \cdot (0.000) = -3.450 \times 10^{-6}$$

$$\Delta D = (1) \cdot (0.000) + (-1) \cdot (0.031) + (-2) \cdot (0.083) = -0.135 \times 10^{-5}$$

$$\text{IDCPH} = \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT = \Delta A \cdot (T - T_0) + \frac{\Delta B}{2} \cdot (T^2 - T_0^2) + \frac{\Delta C}{3} \cdot (T^3 - T_0^3) + \Delta D \cdot \left(\frac{T - T_0}{T \cdot T_0} \right) = -1615.46 \text{ K}$$

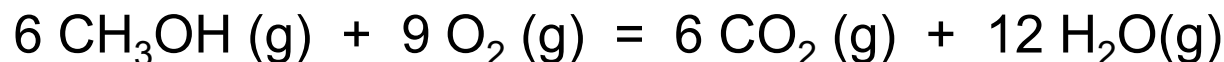
Eq. 4.20

$$\Delta H^{\circ} = \Delta H_{298}^{\circ} + R \cdot \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT = \Delta H_{298}^{\circ} + R \cdot \text{IDCPH} = -90,135 + 8.314 \cdot (-1615.46) = -103,566 \text{ J}$$

Eq. 4.19

Example (4.20 from PS6)

Calculate the standard heat of combustion of 6 moles of methanol at 800 °C with CO₂ and H₂O (g) as products.



$$\Delta H_{298}^{\circ} = \sum_i v_i H_{f,i}^{\circ} = (6) \cdot (-393,509) + (12) \cdot (-241,818) + (-6) \cdot (-200,660) + (-9) \cdot (0) = -4,058,910 \text{ J} \quad \text{Eq. 4.15}$$

| i | v _i | A | Bx10 ³ | Cx10 ⁶ | Dx10 ⁻⁵ |
|--------------------|----------------|-------|-------------------|-------------------|--------------------|
| CO ₂ | 6 | 5.457 | 1.045 | 0.000 | -1.157 |
| H ₂ O | 12 | 3.470 | 1.450 | 0.000 | 0.121 |
| CH ₃ OH | -6 | 2.211 | 12.216 | -3.450 | 0.000 |
| O ₂ | -9 | 3.639 | 0.506 | 0.000 | -0.227 |

$$\Delta A = (6) \cdot (5.547) + (12) \cdot (3.470) + (-6) \cdot (2.211) + (-9) \cdot (3.639) = 28.365$$

$$T_1 = 800 \text{ °C} = 1073 \text{ K}$$

$$\Delta B = (6) \cdot (1.045) + (12) \cdot (1.450) + (-6) \cdot (12.216) + (-9) \cdot (0.506) = -54.180 \times 10^{-3}$$

$$T_0 = 25 \text{ °C} = 298 \text{ K}$$

$$\Delta C = (6) \cdot (0.000) + (12) \cdot (0.000) + (-6) \cdot (3.450) + (-9) \cdot (0.000) = 20.700 \times 10^{-6}$$

$$\Delta D = (6) \cdot (-1.157) + (12) \cdot (0.121) + (-6) \cdot (0.000) + (-9) \cdot (-0.227) = -0.345 \times 10^5$$

$$\text{IDCPH} = \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT = \Delta A \cdot (T - T_0) + \frac{\Delta B}{2} \cdot (T^2 - T_0^2) + \frac{\Delta C}{3} \cdot (T^3 - T_0^3) + \Delta D \cdot \left(\frac{T - T_0}{T \cdot T_0} \right) = 702.64 \text{ K}$$

Eq. 4.20

$$\Delta H^{\circ} = \Delta H_{298}^{\circ} + R \cdot \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT = \Delta H_{298}^{\circ} + R \cdot \text{IDCPH} = -4,058,910 + 8.314 \cdot (702.64) = -4,053,068 \text{ J}$$

Eq. 4.19

Questions?