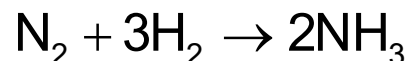


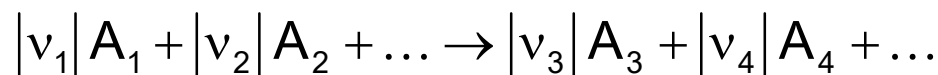
# CH365 Chemical Engineering Thermodynamics

## Lesson 18 Temperature Dependence of $\Delta H^\circ$

# Chemical Reactions



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



$A_i$  = chemical formula

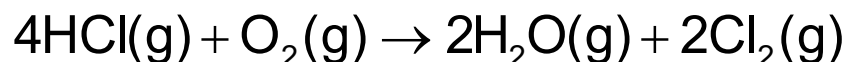
$|v_i|$  = stoichiometric coefficient

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  $T_{\text{ref}}$

# 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

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

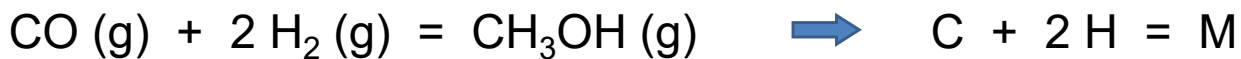
Looks like ICPH and MCPH from  
lesson 16 (slide 4)

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

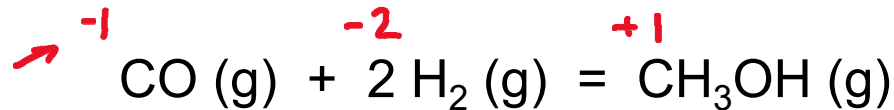
Method: write Cp integrals for each species, add standard heat, reverse order of integration on reactants, replace coefficients with v's, and group integrals together:

$$\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-1: This derivation shows that this equation for calculating  $\Delta H$  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 <sup>3</sup> ✓	Cx10 <sup>6</sup> ✓	Dx10 <sup>-5</sup> ✓
CH <sub>3</sub> OH	✓ 1	2.211	12.216	-3.450	0.000
CO	-1	3.376	0.557	0.000	-0.031
H <sub>2</sub>	-2	3.249	0.422	0.000	0.083

✓ look-up  
Table C.1  
page 656

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

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

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

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

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

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

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

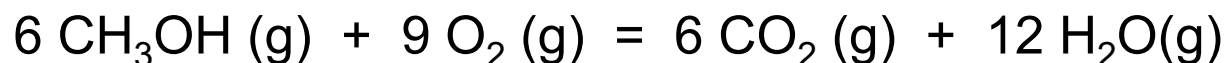
Eq. 4.20

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

Eq. 4.19

# Example L18.1 (4.20 from PS6)

Calculate the standard heat of combustion of 6 moles of methanol at 800 °C with CO<sub>2</sub> and H<sub>2</sub>O (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 <sub>i</sub>	A	Bx10 <sup>3</sup>	Cx10 <sup>6</sup>	Dx10 <sup>-5</sup>
CO <sub>2</sub>	6	5.457	1.045	0.000	-1.157
H <sub>2</sub> O	12	3.470	1.450	0.000	0.121
CH <sub>3</sub> OH	-6	2.211	12.216	-3.450	0.000
O <sub>2</sub>	-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?