CH365 Chemical Engineering Thermodynamics

Lesson 18

Temperature Dependence of ΔH^o

Chemical Reactions

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$\nu_{N_2} = -1 \qquad \nu_{H_2} = -3 \qquad \nu_{NH_3} = +2$$

$$|\nu_1| A_1 + |\nu_2| A_2 + \ldots \rightarrow |\nu_3| A_3 + |\nu_4| A_4 + \ldots$$

$$A_i = \text{chemical formula}$$

$$|\nu_i| = \text{stoichiometric coefficient}$$

positive (+) for products   negative (-) for reactants

$$\Delta H^o = \sum_i \nu_i H_i^o$$ Eq. 4.15

$$\Delta H^o = \sum_i \nu_i H_{f_i}^o$$ Eq. 4.16

$$4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + 2Cl_2(g)$$

$$\Delta H^o = \sum_i \nu_i H_{f_i}^o = 2\Delta H_{f,H_2O}^o - 4\Delta H_{f,HCl}^o$$

BLUF: Need T instead of T_{ref}

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

Standard Reactions

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

Standard reactions are always at P = 1 bar

multiply by ν_i and sum over all i:

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

$$\sum_i d\left(\nu_i H_i^o\right) = \sum_i \nu_i C_{p_i}^o dT$$

$$d\left(\sum_i \left(\nu_i H_i^o\right)\right) = \sum_i \nu_i C_{p_i}^o dT$$

$$\Delta H^o = \sum_i \nu_i H_i^o$$ Eq. 4.15

$$d\Delta H^o = \sum_i \nu_i C_{p_i}^o dT$$

$$\Delta C_P^o \equiv \sum_i \nu_i C_{P_i}^o$$ Eq. 4.17

$$d\Delta H^o = \Delta C_p^o dT$$ Eq. 4.18

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

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

Integrated Forms

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

Eq. 4.20

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

$$\frac{\langle \Delta C_p^o \rangle_H}{R} = \Delta A + \frac{\Delta B}{2} \cdot (T + T_0) + \frac{\Delta C}{3} \cdot (T^2 + T_0^2 + T \cdot T_0) + \frac{\Delta D}{T \cdot T_0}$$

Eq. 4.21

$(T - T_0)$ factored out

$$\Delta H^o = \Delta H_0^o + \langle \Delta C_p^o \rangle_H (T - T_0)$$

Eq. 4.22

Derived on next slide

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

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

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

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

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

Derivation of Integrated Forms at T

$$CO\,(g) + 2\,H_2\,(g) = CH_3OH\,(g) \quad \Rightarrow \quad C + 2\,H = M$$

Important derivation (not in book)

$$\nu_{CO} = -1 = \nu_C \qquad \nu_{H_2} = -2 = \nu_H \qquad \nu_{CH_3OH} = +1 = \nu_M$$

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 ν's, and group integrals together:

$$\Delta H = \underbrace{R\int_{T}^{T_0}\frac{C_P^C}{R}dT + R\int_{T}^{T_0}2\frac{C_P^H}{R}dT}_{\text{cool the reactants}} + \underbrace{\Delta H_R^o}_{\text{react}} + \underbrace{R\int_{T_0}^{T}\frac{C_P^M}{R}dT}_{\text{warm the products}}$$

flip

$$= R\int_{T_0}^{T}-\frac{C_P^C}{R}dT + R\int_{T_0}^{T}-2\frac{C_P^H}{R}dT + R\int_{T_0}^{T}\frac{C_P^M}{R}dT + \Delta H_R^o$$

$$= R\int_{T_0}^{T}\left\{\nu_C\frac{C_P^C}{R} + \nu_H\frac{C_P^H}{R} + \nu_M\frac{C_P^M}{R}\right\}dT + \Delta H_R^o$$

$$= R\int_{T_0}^{T}\left\{\nu_C\left(A_C + B_CT + C_CT^2 + D_CT^{-2}\right) + \nu_H\left(A_H + B_HT + C_HT^2 + D_HT^{-2}\right) + \nu_M\left(A_M + B_MT + C_MT^2 + D_MT^{-2}\right)\right\}dT + \Delta H_R^o$$

$$= R\int_{T_0}^{T}\left\{\nu_CA_C + \nu_CB_CT + \nu_CC_CT^2 + \nu_CD_CT^{-2} + \nu_HA_H + \nu_HB_HT + \nu_HC_HT^2 + \nu_HD_HT^{-2} + \nu_MA_M + \nu_MB_MT + \nu_MC_MT^2 + \nu_MD_MT^{-2}\right\}dT + \Delta H_R^o$$

$$= R\int_{T_0}^{T}\left\{\underbrace{\nu_CA_C + \nu_HA_H + \nu_MA_M}_{\Delta A} + \nu_CB_CT + \nu_HB_HT + \nu_MB_MT + \nu_CC_CT^2 + \nu_MC_MT^2 + \nu_HC_HT^2 + \nu_CD_CT^{-2} + \nu_HD_HT^{-2} + \nu_MD_MT^{-2}\right\}dT + \Delta H_R^o$$

$$\Delta A = \nu_CA_C + \nu_HA_H + \nu_MA_M, \quad \Delta B = \nu_CB_C + \nu_HB_H + \nu_MB_M, \quad \text{etc.}$$

$$= R\int_{T_0}^{T}\left\{\Delta A + \Delta B\cdot T + \Delta C\cdot T^2 + \Delta D\cdot T^{-2}\right\}dT + \Delta H_R^o$$

$$= R\int_{T_0}^{T}\frac{\Delta C_P}{R}dT + \Delta H_R^o = R\cdot IDCPH + \Delta H_R^o$$

(BLUF^{-1}: 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.

$$\overset{-1}{CO\,(g)} + \overset{-2}{2\,H_2\,(g)} = \overset{+1}{CH_3OH\,(g)}$$

$$\Delta H^o_{298} = \sum_i \nu_i H^o_{f_i} = (1)\cdot(-200{,}660) + (-1)\cdot(-110{,}525) = -90{,}135\,J$$ Eq. 4.16

i	ν_i	A	Bx10³	Cx10⁶	Dx10⁻⁵
CH_3OH	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
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$$\Delta A = (1)\cdot(2.211) + (-1)\cdot(3.376) + (-2)\cdot(3.249) = -7.663$$

$$\Delta B = (1)\cdot(12.216) + (-1)\cdot(0.557) + (-2)\cdot(0.422) = 10.815\times10^{-3}$$

$$\Delta C = (1)\cdot(-3.450) + (-1)\cdot(0.000) + (-2)\cdot(0.000) = -3.450\times10^{-6}$$

$$\Delta D = (1)\cdot(0.000) + (-1)\cdot(0.031) + (-2)\cdot(0.083) = -0.135\times10^{5}$$

$$T = 800\,^oC = 1073K$$

$$T_0 = 25\,^oC = 298K$$

$$IDCPH = \int_{T_0}^{T} \frac{\Delta C^o_p}{R} dT = \Delta A\cdot(T - T_0) + \frac{\Delta B}{2}\cdot(T^2 - T_0^2) + \frac{\Delta C}{3}\cdot(T^3 - T_0^3) + \Delta D\cdot\left(\frac{T - T_0}{T\cdot T_0}\right) = -1615.46K$$ Eq. 4.20

$$\Delta H^o = \Delta H^o_{298} + R\cdot\int_{T0}^{T} \frac{\Delta C^o_P}{R} dT = \Delta H^o_{298} + R\cdot IDCPH = -90{,}135 + 8.314\cdot(-1615.46) = -103{,}566\,J$$ Eq. 4.19

Example L18.1 (4.20 from PS6)

Calculate the standard heat of combustion of 6 moles of methanol at 800 ^oC with CO_2 and H_2O (g) as products.

$$6\ CH_3OH\ (g)\ +\ 9\ O_2\ (g)\ =\ 6\ CO_2\ (g)\ +\ 12\ H_2O(g)$$

$$\Delta H^o_{298} = \sum_i \nu_i H^o_{f_i} = (6)\cdot(-393{,}509) + (12)\cdot(-241{,}818) + (-6)\cdot(-200{,}660) + (-9)\cdot(0) = -4{,}058{,}910\ \mathrm{J}$$ Eq. 4.15

i	ν_i	A	Bx10^3	Cx10^6	Dx10^{-5}
CO_2	6	5.457	1.045	0.000	-1.157
H_2O	12	3.470	1.450	0.000	0.121
CH_3OH	-6	2.211	12.216	-3.450	0.000
O_2	-9	3.639	0.506	0.000	-0.227

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

$$\Delta B = (6)\cdot(1.045) + (12)\cdot(1.450) + (-6)\cdot(12.216) + (-9)\cdot(0.506) = -54.180\times10^{-3}$$

$$\Delta C = (6)\cdot(0.000) + (12)\cdot(0.000) + (-6)\cdot(3.450) + (-9)\cdot(0.000) = 20.700\times10^{-6}$$

$$\Delta D = (6)\cdot(-1.157) + (12)\cdot(0.121) + (-6)\cdot(0.000) + (-9)\cdot(-0.227) = -0.345\times10^{5}$$

$$T_1 = 800\ ^oC = 1073\mathrm{K}$$

$$T_0 = 25\ ^oC = 298\mathrm{K}$$

$$\mathrm{IDCPH} = \int_{T_0}^{T} \frac{\Delta C_p^o}{R} dT = \Delta A\cdot(T - T_0) + \frac{\Delta B}{2}\cdot(T^2 - T_0^2) + \frac{\Delta C}{3}\cdot(T^3 - T_0^3) + \Delta D\cdot\left(\frac{T - T_0}{T\cdot T_0}\right) = 702.64\,\mathrm{K}$$ Eq. 4.20

$$\Delta H^o = \Delta H^o_{298} + R\cdot\int_{T0}^{T} \frac{\Delta C_P^o}{R} dT = \Delta H^o_{298} + R\cdot \mathrm{IDCPH} = -4{,}058{,}910 + 8.314\cdot(702.64) = -4{,}053{,}068\mathrm{J}$$ Eq. 4.19

Questions?