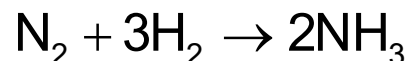# CH365 Chemical Engineering Thermodynamics
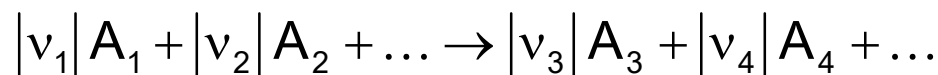
Lesson 18
Temperature Dependence of ΔH^o

Professor Andrew Biaglow
3 October 2022

Chemical Reactions

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

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

$$|\nu_1|A_1 + |\nu_2|A_2 + \ldots \rightarrow |\nu_3|A_3 + |\nu_4|A_4 + \ldots$$
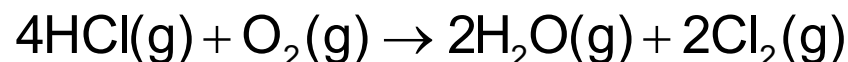
$$A_i = \text{chemical formula}$$

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

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

$$\Delta H^o = \sum_i \nu_i H_i^o \quad \text{Eq. 4.15} \qquad \Delta H^o = \sum_i \nu_i H_{f_i}^o \quad \text{Eq. 4.16}$$

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

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

BLUF: Need T instead of T_{ref}

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

Standard Reactions

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

Standard reactions are always at P = 1 bar

multiply by ν_i and sum over all i:

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

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

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

Eq. 4.15

$$d\Delta H^o = \sum_i \nu_i C_{p_i}^o dT \qquad \Delta C_P^o \equiv \sum_i \nu_i C_{P_i}^o$$

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

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

$(T - T_0)$ factored out

Eq. 4.22

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

Derived on next slide

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

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

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

Derivation of Integrated Forms at T
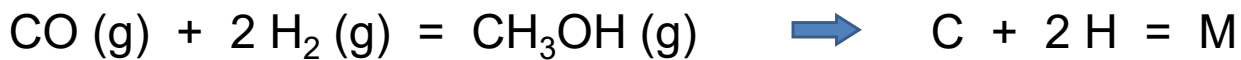
$$CO\ (g)\ +\ 2\,H_2\ (g)\ =\ CH_3OH\ (g) \quad \Rightarrow \quad C\ +\ 2\,H\ =\ M$$

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:

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

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

$$= R\int_{T_0}^T\left\{\nu_C\left(A_C + B_C T + C_C T^2 + D_C T^{-2}\right) + \nu_H\left(A_H + B_H T + C_H T^2 + D_H T^{-2}\right) + \nu_M\left(A_M + B_M T + C_M T^2 + D_M T^{-2}\right)\right\}dT + \Delta H_R^o$$

$$= R\int_{T_0}^T\left\{\nu_C A_C + \nu_C B_C T + \nu_C C_C T^2 + \nu_C D_C T^{-2} + \nu_H A_H + \nu_H B_H T + \nu_H C_H T^2 + \nu_H D_H T^{-2} + \nu_M A_M + \nu_M B_M T + \nu_M C_M T^2 + \nu_M D_M T^{-2}\right\}dT + \Delta H_R^o$$

$$= R\int_{T_0}^T\left\{\underbrace{\nu_C A_C + \nu_H A_H + \nu_M A_M}_{\Delta A} + \nu_C B_C T + \nu_H B_H T + \nu_M B_M T + \nu_C C_C T^2 + \nu_M C_M T^2 + \nu_H C_H T^2 + \nu_C D_C T^{-2} + \nu_H D_H T^{-2} + \nu_M D_M T^{-2}\right\}dT + \Delta H_R^o$$

$$\Delta A = \underbrace{\nu_C A_C + \nu_H A_H + \nu_M A_M}, \quad \Delta B = \nu_C B_C + \nu_H B_H + \nu_M B_M, \quad \text{etc.}$$

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

The important result of this derivation is that this only works when T is the same for reactants and products.

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

Example 4.6

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

$$CO\ (g)\ +\ 2\ H_2\ (g)\ =\ CH_3OH\ (g)$$

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

i	ν_i	A	Bx10³	Cx10⁶	Dx10⁻⁵
CH₃OH	1	2.211	12.216	-3.450	0.000
CO	-1	3.376	0.557	0.000	-0.031
H₂	-2	3.249	0.422	0.000	0.083

Table C.1
page 656

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

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

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

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

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

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

$$IDCPH = \int_{T_0}^{T} \frac{\Delta C^o_P}{R}dT = \Delta A\cdot(T-T_0) + \frac{\Delta B}{2}\cdot(T^2-T_0^2) + \frac{\Delta C}{3}\cdot(T^3-T_0^3) + \Delta D\cdot\left(\frac{T-T_0}{T\cdot T_0}\right) = -1615.46K$$
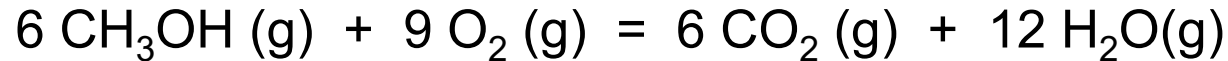
$$\Delta H^o = \Delta H^o_{298} + R\cdot\int_{T0}^{T}\frac{\Delta C^o_P}{R}dT = \Delta H^o_{298} + R\cdot IDCPH = -90,135 + 8.314\cdot(-1615.46) = -103,566\,J$$

Example L18.1 (from PS6)

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

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

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

i	ν_i	A	Bx10³	Cx10⁶	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

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

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

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

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

$$T_1 = 800\,^oC = 1073K$$

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

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

Eq. 4.20

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

Eq. 4.19

Homework

Problem 4.22

What is the standard heat of combustion of n-pentane gas at 25 ^{o}C if the combustion products are $H_2O(l)$ and $CO_2(g)$?

Problem 4.28

Natural gas (assume pure methane) is delivered to a city via pipeline at a volumetric flow rate of 150 million standard cubic feet per day. If the selling price of the gas is $5.00 per GJ of higher heating value, what is the expected revenue in dollars per day? Standard conditions are 60 deg F and 1 atm.

Problem 4.71

Locate your name in the list below and use the DIPPR database to find the critical temperature and pressure for the compounds assigned to you. Report your results in units of bar and K. What does DIPPR stand for, who created it, and when?

Dawson	sodium chloride	chlorine dioxide	isoquinoline
Harrison	bisphenol	cyanogen chloride	acetoacetanilide
Lucero	chlorine	chlorine trifluoride	p-cymene
Romsland	piperazine	anisole	triethyl phosphate
Tuttle	pyridine	trans-2-hexene	naphthalene
Bedor	cis-2-hexene	methyl iodide	n-undecane
Bomke	cis-3-hexene	acetaldoxime	phosgene
Hawang	methyl methacrylate	2-chloroethanol	diethyl sulfide
Komorowski	allyl alcohol	diethanolamine	ammonium sulfide
Liesen	iodine	crotyl glycol ether	methyl mercaptan
Sawyer	quinoline	2-mercaptoethanol	pyrazine
Taptich	acridine	ethylthioethanol	pyrazole
Zlotnick	niacin	thiodiglycol	isoxazole

Problem 4.83

Hydrocarbon fuels such as methanol are used to store energy in liquid form. Flow calorimeters are frequently used to measure standard heats of reaction for liquid fuels. An example is shown on page 54. Use CHEMCAD to construct a simulation of a flow calorimeter that is designed to combust methanol in a stoichiometric amount of air.

The feed mixture enters the process at 20 deg C and must be preheated to 25 deg C before entering the reactor. The reactor effluent must be cooled to 25 deg C before discharge to the atmosphere.

Compare the heat of reaction from CHEMCAD to the value obtained in Problem 4.20.

(Submit your CHEMCAD file to your SharePoint directory.)