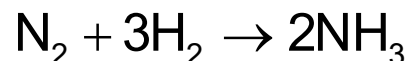


CH365 Chemical Engineering Thermodynamics

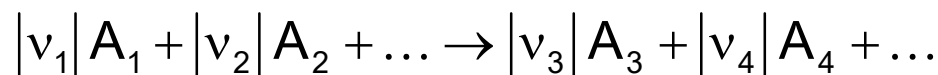
Lesson 18

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

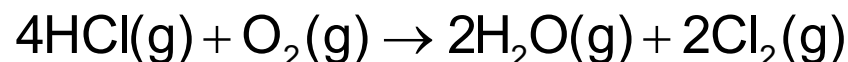
$|v_i|$ = stoichiometric coefficient

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

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

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

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

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

Eq. 4.22

Derived on
next slide

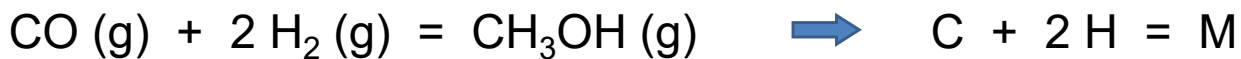
$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \text{IDCPH}$$

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

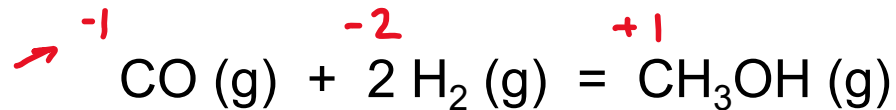
Method: write Cp integrals for each species, add standard heat, reverse order of integration on reactants, replace coefficients with v's, and group integrals together:

$$\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 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

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

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

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

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

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

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

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

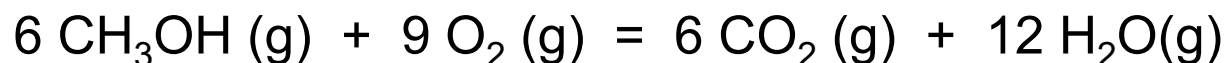
Eq. 4.20

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

Eq. 4.19

Example L18.1 (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

$$\Delta A = (6) \cdot (5.457) + (12) \cdot (3.470) + (-6) \cdot (2.211) + (-9) \cdot (3.639) = 28.365$$

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

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

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

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

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

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

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

Homework

Problem 4.22

What is the standard heat of combustion of n-pentane gas at 25 °C if the combustion products are $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$?

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?

Baldwin	sodium chloride	chlorine dioxide	isoquinoline
Behr	bisphenol A	cyanogen chloride	acetoacetanilide
Benson	chlorine	chlorine trifluoride	p-cymene
Cianfaglione	piperazine	anisole	triethyl phosphate
Ibrahimi	pyridine	trans-2-hexene	naphthalene
Milanesa	acetone	sulfur dichloride	benzonitrile
Morrall	ethyl acetate	benzonitrile	camphor
Mossman	sodium hydroxide	silicon dioxide	cumene
Murray	1,3 dioxane	2-butanol	carbon monoxide
Onaga	ethanol	anethole	dibenzyl ether
Weaver	benzene	trans-3-hexene	cetane
Bennett, S	cis-3-hexene	acetaldoxime	phosgene
Cesarski	methyl methacrylate	2-chloroethanol	diethyl sulfide
Dolin	allyl alcohol	diethanolamine	ammonium sulfide
Goulet	iodine	crotyl glycol ether	methyl mercaptan
Johnson	quinoline	2-mercaptoethanol	pyrazine
Kotkin	acridine	ethylthioethanol	pyrazole
Patel	niacin	thiodiglycol	isoxazole
Sullivan	acrylonitrile	triethanolamine	caprolactam
Weathers	fluorine	triethylene glycol	cetyl methacrylate
Williams	n-tricosane	allyl methacrylate	graphite

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.)