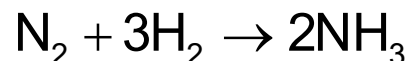


CH365 Chemical Engineering Thermodynamics

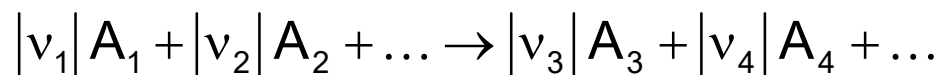
Lesson 18 Temperature Dependence of ΔH°

BLUF: Need T instead of T_{ref}

Chemical Reactions



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



A_i = chemical formula

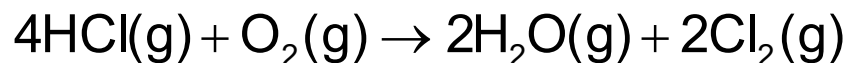
$|v_i|$ = stoichiometric coefficient

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

$$\frac{\langle \Delta C_p^\circ \rangle_H}{R} = \text{MDCPH} \quad \text{In book: MDCPH}(T_0, T, DA, DB, DC, DD)$$

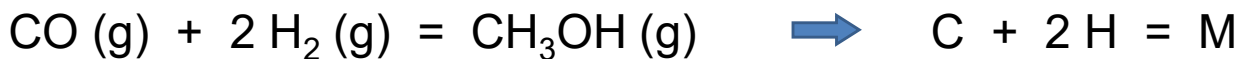
Looks like MCPH from lesson 16

Derived on
next slide

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \text{IDCPH} \quad \text{In book: IDCPH}(T_0, T, DA, DB, DC, DD)$$

Looks like ICPH from lesson 16

Derivation of Integrated Forms at T Slide 5



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

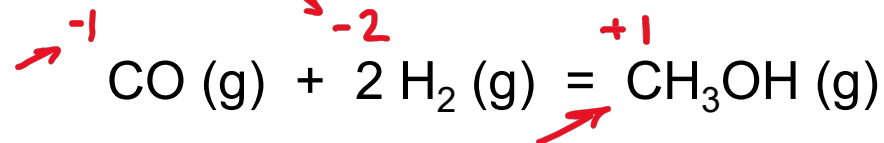
Method: write C_p integrals for each species, add standard heat, reverse order of integration on reactants, replace coefficients with v 's, group integrals together, and collect terms:

$$\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 -\frac{C_P^{\text{C}}}{R} dT + R \int_{T_0}^T -2 \frac{C_P^{\text{H}}}{R} dT + R \int_{T_0}^T \frac{C_P^{\text{M}}}{R} dT + \Delta H_{\text{R}}^{\circ} \\ &= 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

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

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

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

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

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

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

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

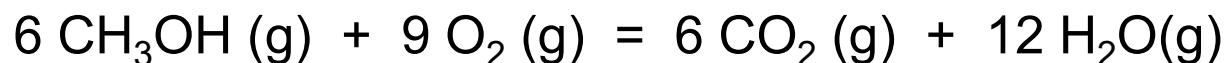
Eq. 4.20

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

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

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

$$T_1 = 800 \text{ }^{\circ}\text{C} = 1073 \text{ K}$$

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

$$T_0 = 25 \text{ }^{\circ}\text{C} = 298 \text{ K}$$

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

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

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

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?

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 °F and 1 atm.

Problem 4.53

Saturated water vapor, i.e., *steam*, is commonly used as a heat source in heat exchanger applications. Why *saturated* water vapor? Why *saturated water* vapor?

In a plant of any reasonable size, several varieties of saturated steam are commonly available. For example, saturated steam may be available at 4.5, 9, 17, and 33 bar. But the higher the pressure, the lower the useful energy content and the greater the cost. Why is the energy content lower at higher pressure? Why then is higher-pressure steam used?

Problem 4.54

The oxidation of glucose provides the principal source of energy for animal cells. Assuming the reactants are glucose [$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$] and oxygen [$\text{O}_2(\text{g})$] and the products are $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, answer the following:

- (a) Write a balanced equation for glucose oxidation, and determine the standard heat of reaction at 298 K.
- (b) During a day, an average person consumes about 150 kJ of energy per kg of body mass. Assuming glucose is the only source of energy, estimate the mass (grams) of glucose required daily to sustain a person of 57 kg.
- (c) For a population of 275 million people, what mass of CO_2 (a greenhouse gas) is produced daily by mere respiration? Data: for glucose, $\Delta H_{\text{f},298}^0 = -1,274,4 \text{ kJ/mol}$. Ignore the effect of temperature on the heat of reaction.