

Chemistry 163B Winter 2020

Lectures 6-7 Thermochemistry

Chemistry 163B

Lectures 6-7

Thermochemistry

Chapter 4 Engel & Reid

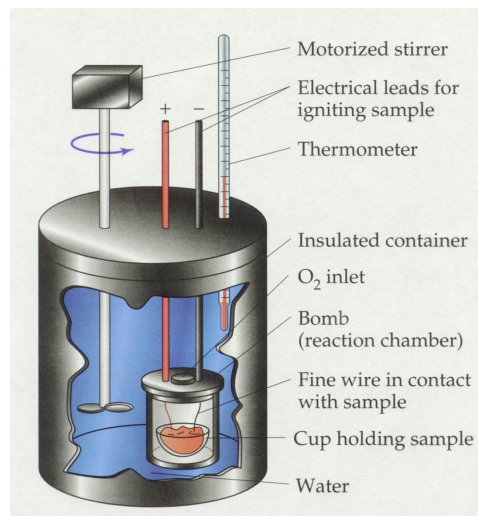
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1

heats of reactions (constant volume; 'bomb' calorimeter)

$$\Delta U_V = q_V$$

$$\Delta U = U_{\text{products}} - U_{\text{reactants}}$$



2

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heats of reactions (constant volume; fig 4.3 E&R_{4th}) [4.3]3rd

$$\Delta U_V = q_V$$

$$\Delta U = U_{\text{products}} - U_{\text{reactants}}$$

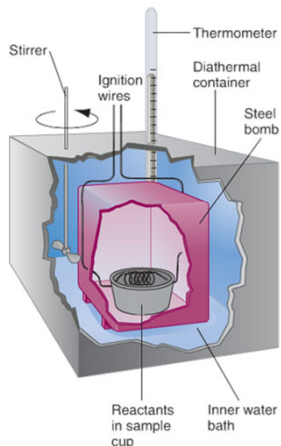


FIGURE 4.3

FIGURE 4.3 Schematic diagram of a bomb calorimeter. The liquid or solid reactant is placed in a cup suspended in the thick-walled steel bomb, which is filled with O₂ gas. The vessel is immersed in an inner water bath, and its temperature is monitored. The diathermal container is immersed in an outer water bath (not shown) whose temperature is maintained at the same value as the inner bath through a heating coil. By doing so, there is no heat exchange between the inner water bath and the rest of the universe.

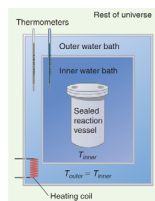


FIGURE 2.3 An isolated composite system is created in which the surroundings to the system of interest are limited in extent. The walls surrounding the inner water bath are rigid.

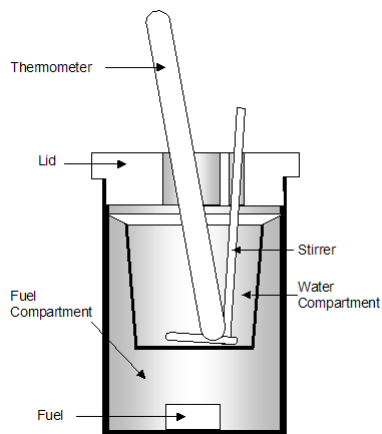
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3

heats of reactions (constant pressure; 'coffee cup calorimeter')

$$\Delta H_P = q_P$$

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



4

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heats of reactions (constant pressure; fig 4.4 E&R_{4th}) [4.4]3rd

$$\Delta H_p = q_p$$

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

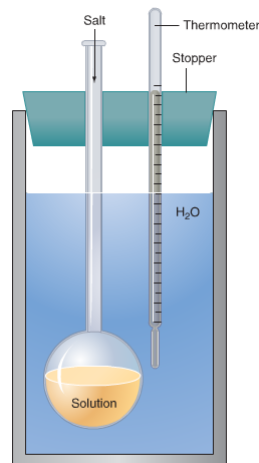
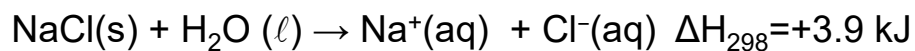
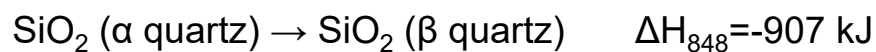
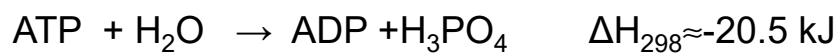
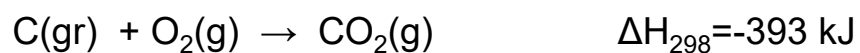


FIGURE 4.4
Schematic diagram of a constant pressure calorimeter suitable for measuring the enthalpy of solution of a salt in water.

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most reactions at P constant, $\Delta H_p = q_p$



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topics for thermochemistry, parts of Ch. 4 Engel & Reid

- HW#3 16,17,18** • Calculate $\Delta H_{\text{reaction}}$
Hess's Law, standard heats of formation
- HW#3 16,21** • $\Delta H_{\text{reaction}}$ vs $\Delta U_{\text{reaction}}$
- HW#3 18, *19** • Temperature (*and later* pressure) dependence
of $\Delta H_{\text{reaction}}$
 - Calorimetry
 - Heats of solution
- HW#3 20** • $\Delta H_{\text{reaction}}$ from bond enthalpies

----- MIDTERM 1 -----

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Hess's Law

$$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$$

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ΔH State Function ⇒ Hess's Law

can't measure directly

$$\text{O}_2(\text{g}) + \text{C}(\text{gr}) \xrightarrow[\Delta H_{\text{I}}=?]{\text{I}} \text{C}(\text{dia}) + \text{O}_2(\text{g})$$

$\Delta H_{\text{II}} = \Delta H_{\text{combustion}}(\text{gr})$

II

$\Delta H_{\text{III}} = -\Delta H_{\text{combustion}}(\text{dia})$

III

$\text{CO}_2(\text{g})$

$\Delta H_{\text{I}} = \Delta H_{\text{II}} + \Delta H_{\text{III}}$

| | | | ΔH kJ |
|-------------------------|---|--|---------------|
| ΔH_{I} | $\text{C}(\text{gr}) \rightarrow \text{C}(\text{dia})$ | | ? |
| \parallel | | | |
| ΔH_{II} | $\text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ | | -393.51 |
| + | | | |
| ΔH_{III} | $\text{CO}_2(\text{g}) \rightarrow \text{C}(\text{dia}) + \text{O}_2(\text{g})$ | | +395.41 |

$\Delta H_{\text{I}} = \Delta H_{\text{II}} + \Delta H_{\text{III}} = 1.90 \text{ kJ}$

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factors affecting $\Delta H_{\text{reaction}}$

- stoichiometry
 ΔH is extensive; $\Delta \bar{H}$ is intensive
- physical state
phase or crystal form of reactants and products
- temperature and pressure
- does **NOT** depend on path

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notation: ΔH (etc) in terms of molar enthalpies and stoichiometric coefficients



$$H_{\text{prods}} = \sum_{i=\text{prods}} n_i \bar{H}_i \quad H_{\text{reacts}} = \sum_{i=\text{reacts}} n_i \bar{H}_i$$

$$\Delta H_{\text{reaction}} = \sum_{i=\text{prods}} n_i \bar{H}_i - \sum_{i=\text{reacts}} n_i \bar{H}_i$$

total enthalpy of reactants
molar enthalpy of reactant i
number of moles of i in stoichiometry

v_i is stoichiometric coefficient of i^{th} reactant / product

$v_i = n_i$ if i is product species

$v_i = -n_i$ if i is reactant species

$$\Delta H_{\text{reaction}} = \sum_i v_i \bar{H}_i$$

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$\Delta H_{\text{reaction}}$ vs $\Delta U_{\text{reaction}}$ at fixed temperature T

$$H \equiv U + PV$$

$$\Delta H = H_{\text{prods}} - H_{\text{reacts}}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (PV)_{\text{prods}} - (PV)_{\text{reacts}}$$

assume:

i) PV and ΔPV is small for solids and liquids

ii) Gasses follow ideal gas law

$$\Delta PV = (PV)_{\text{prods}} - (PV)_{\text{reacts}}$$

$$\Delta PV = (n_{\text{gas}} RT)_{\text{prod}} - (n_{\text{gas}} RT)_{\text{react}}$$

$$\Delta PV = \Delta n_{\text{gas}} RT$$

$$\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta n_{\text{gas}} RT$$

E&R_{4th} eqn 4.23 ??

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standard states and enthalpies of formation (0, 1 mol $\equiv \ominus$ E&R)

$\Delta \bar{H}^\circ(T, P = 1 \text{ atm [or 1 bar]})$

standard state

often T is assumed 298K for standard ("reference") state
 $\Delta \bar{H}^\circ_{298}$

define standard states \Rightarrow

$(\Delta \bar{H}^\circ_{298})_{\text{formation}} \equiv \bar{H}_f^\circ$
molar enthalpy of formation

define enthalpy of formation \Rightarrow

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$\Delta H^\circ_{\text{rxn}}$ from H_f°

reactants \rightarrow products

$(-\Delta H_f^\circ)_{\text{reactants}}$
 $(\Delta H_f^\circ)_{\text{products}}$

elements in most stable state

$$(\Delta H^\circ)_{\text{rxn}} = \sum_i \nu_i (\bar{H}_f^0)_i$$

do HW#3 problem 16b (E&R P4.33b)

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topics for thermochemistry, parts of Ch. 4 E&R

- ✓ • Calculate $\Delta H_{\text{reaction}}$
Hess's Law, standard heats of formation
- ✓ • $\Delta H_{\text{reaction}}$ vs $\Delta U_{\text{reaction}}$
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- Heats of solution
- $\Delta H_{\text{reaction}}$ from bond enthalpies

MIDTERM 1

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temperature dependence of H of substance at constant P

$$dH = n\bar{C}_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

for a given reactant or product at constant P

$$dH_p = n\bar{C}_p dT \quad d\bar{H}_p = \bar{C}_p dT$$

$$\int_{T_1}^{T_2} d\bar{H} = \int_{T_1}^{T_2} \bar{C}_p dT$$

$$\bar{H}(T_2) - \bar{H}(T_1) = \int_{T_1}^{T_2} \bar{C}_p dT$$

$$\bar{H}(T_2) = \bar{H}(T_1) + \int_{T_1}^{T_2} \bar{C}_p dT$$

change in
enthalpy of
substance
 $T_1 \rightarrow T_2$

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temperature dependence of $\Delta H_{\text{reaction}}$ (reaction carried out at constant P, T)

$$\Delta H_{\text{reaction}} = \sum_i \nu_i \bar{H}_i \quad (\Delta C_p)_{\text{reaction}} = \sum_i \nu_i (\bar{C}_p)_i \quad \Delta H_{\text{rxn}}(T_1, P)$$

vs

$$\bar{H}_i(T_2) = \bar{H}_i(T_1) + \int_{T_1}^{T_2} (\bar{C}_p)_i dT \quad \Delta H_{\text{rxn}}(T_2, P)$$

$$\Delta H_{\text{reaction}}(T_2) = \sum_j \nu_j \bar{H}_j(T_2)$$

$$\sum_j \nu_j \bar{H}_j(T_2) = \sum_j \nu_j \bar{H}_j(T_1) + \sum_i \nu_i \int_{T_1}^{T_2} (\bar{C}_p)_i dT$$

$$\Delta H_{\text{reaction}}(T_2) = \Delta H_{\text{reaction}}(T_1) + \int_{T_1}^{T_2} \sum_i \nu_i (\bar{C}_p)_i dT$$

change of ΔH_{rxn}
 $T_1 \rightarrow T_2$

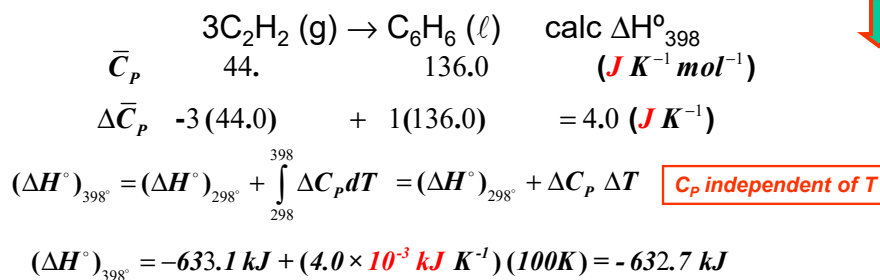
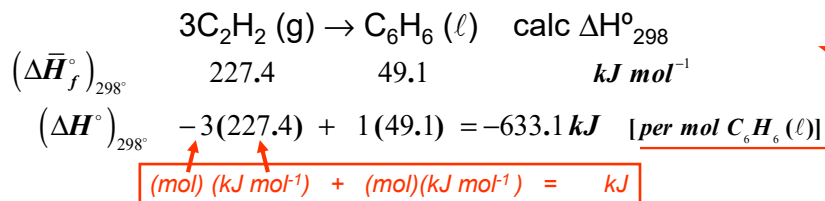
$$\Delta H_{\text{reaction}}(T_2) = \Delta H_{\text{reaction}}(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

where $\Delta C_p = \sum_i \nu_i (\bar{C}_p)_i = "(C_p)_{\text{products}} - (C_p)_{\text{reactants}}"$

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example problems : ΔH from H_f and ΔH $T=298K \Rightarrow 398K$



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- ✓ • $\Delta H_{\text{reaction}}$ vs $\Delta U_{\text{reaction}}$
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- Calorimetry
- Heats of solution
- $\Delta H_{\text{reaction}}$ from bond enthalpies

----- MIDTERM 1 -----

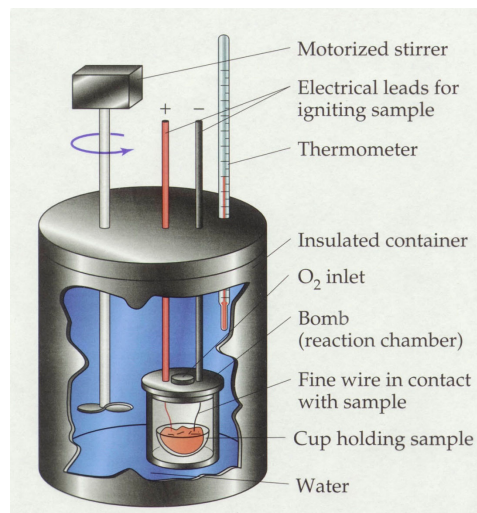
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heats of reactions (constant volume)

$$\Delta U_V = q_V$$

$$\Delta U = U_{\text{products}} - U_{\text{reactants}}$$



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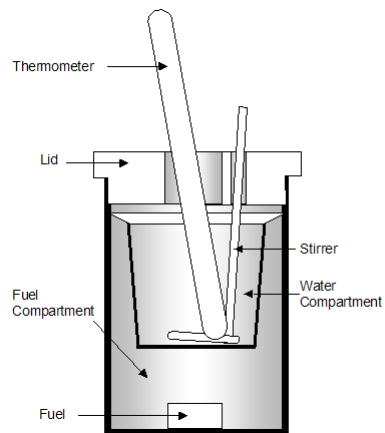
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heats of reactions (constant pressure)

$$\Delta H_p = q_p$$
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



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DSC- differential scanning calorimetry (enrichment, don't FRET)



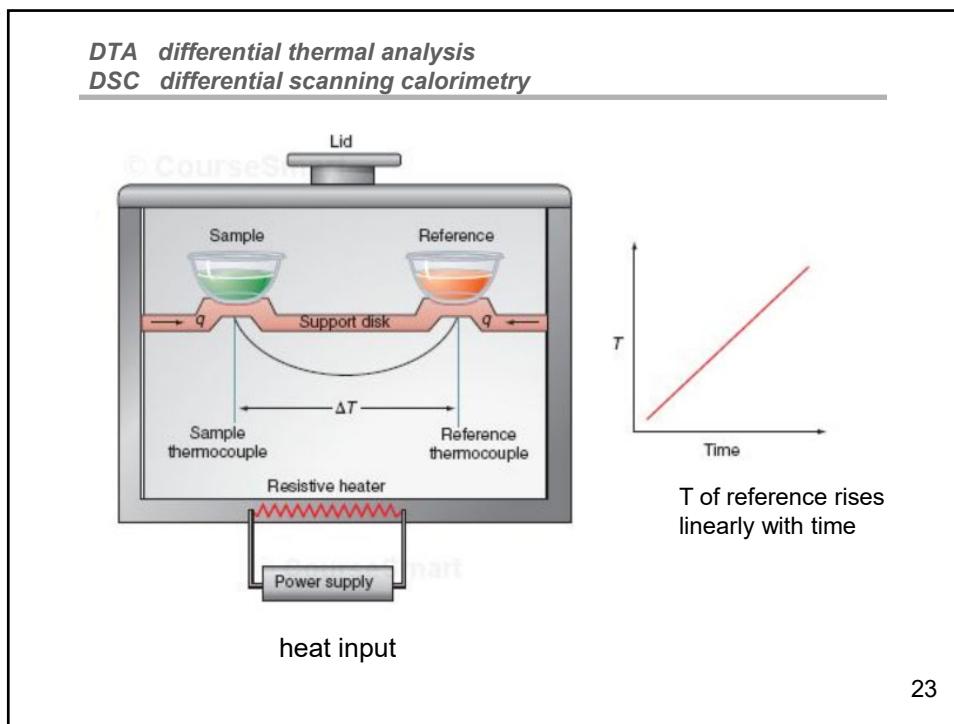
useful for small samples (often biological)

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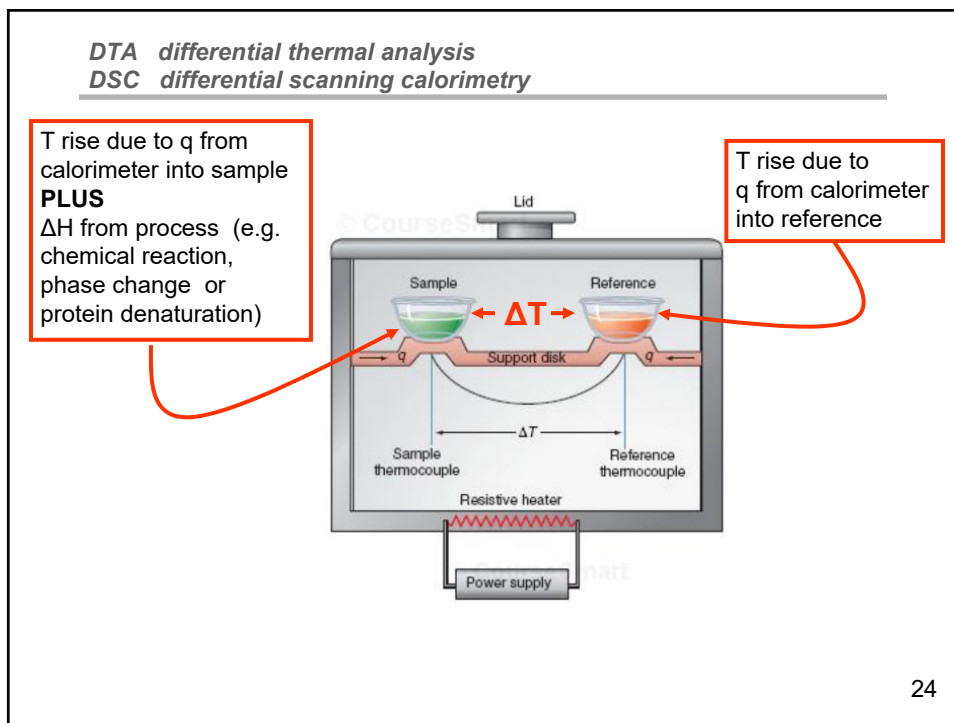
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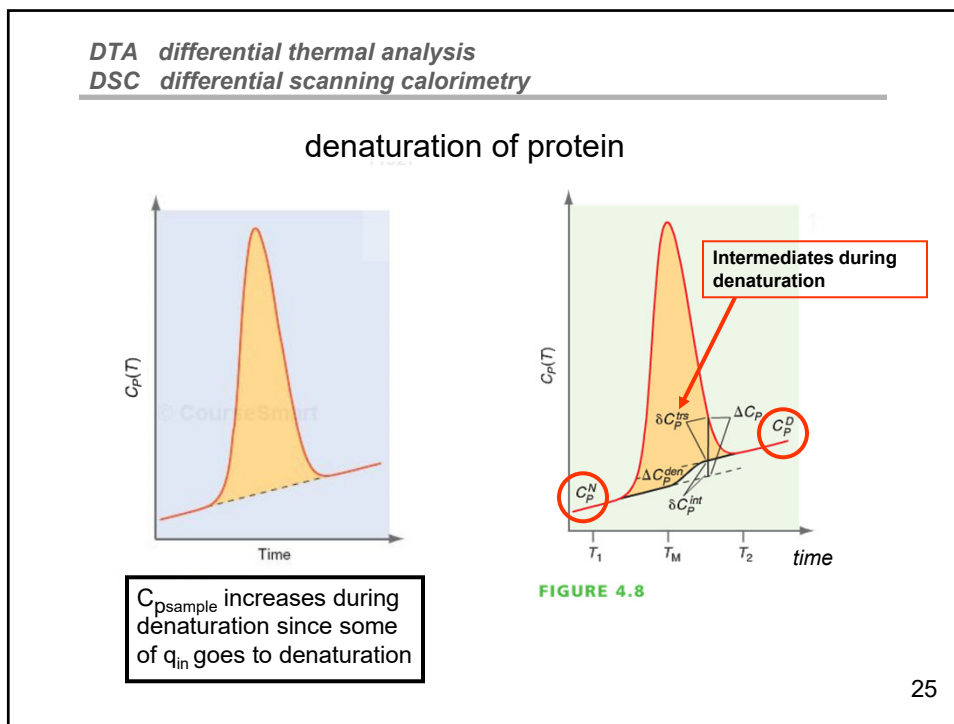
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how H and ΔH change with pressure (don't FRET now)

will prove later:

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \bar{V} - T \left(\frac{\partial \bar{V}}{\partial T}\right)_P = \bar{V} - T\bar{V}\alpha$$

$\alpha \equiv \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T}\right)_P$ the coefficient of thermal expansion

$$\left(\frac{\partial \Delta H_{\text{reaction}}}{\partial P}\right)_T = \sum_i \nu_i (\bar{V}_i - T\bar{V}_i \alpha_i)$$

Will show later:

dependence of $\Delta H_{\text{reaction}}$ on pressure is usually weak

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heats of formation of ions (heat of solutions), (Example 4.4 p 73)_{3rd}

importance: how to assign \bar{H}_f^0 for an individual ion in solution since ions come in 'pairs'

resolution: assign $\bar{H}_f^0(\text{H}^+(\text{aq}, 1\text{M})_{\text{ideal}}) = 0$

and measure \bar{H}_f^0 for other ions relative to H^+

another importance: HW3 #21 E&R_{4th} P4.5d

21. P4.5 Calculate $\Delta_r H^\circ$ and $\Delta_r U^\circ$ at 298.15 K for the following reactions:
d. $2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

Assume complete dissociation of NaOH, H_2SO_4 , and Na_2SO_4 .

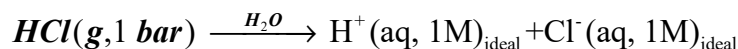
$$\begin{aligned} \Delta H_{\text{reaction}} = & -2\cancel{\Delta\bar{H}_f^0(\text{Na}^+)} - 2\cancel{\Delta\bar{H}_f^0(\text{OH}^-)} - 2\cancel{\Delta\bar{H}_f^0(\text{H}^+)} - \cancel{\Delta\bar{H}_f^0(\text{SO}_4^{2-})} \\ & + 2\cancel{\Delta\bar{H}_f^0(\text{Na}^+)} + \cancel{\Delta\bar{H}_f^0(\text{SO}_4^{2-})} + 2\Delta\bar{H}_f^0(\text{H}_2\text{O}) \end{aligned}$$

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heats of formation of ions (heat of solutions)

HOW TO GET $\Delta\bar{H}_f^0$ for $\text{Cl}^-(\text{aq})$



$$\Delta H_{\text{measured}} = -74.9 \text{ kJ}$$

$$-74.9 \text{ kJ} = -\Delta\bar{H}_f^0(\text{HCl}(\text{g})) + \Delta\bar{H}_f^0(\text{H}^+(\text{aq})) + \Delta\bar{H}_f^0(\text{Cl}^-(\text{aq}))$$

$$-74.9 \text{ kJ} = -(-92.3 \text{ kJ}) + 0 + \bar{H}_f^0(\text{Cl}^-(\text{aq}))$$

$$\Delta\bar{H}_f^0(\text{Cl}^-(\text{aq})) = -167.2 \text{ kJ mol}^{-1}$$

GOT $\Delta\bar{H}_f^0$ for $\text{Cl}^-(\text{aq})$

NOW

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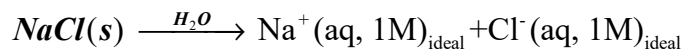
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heats of formation of ions (heat of solutions)

GET $\Delta\bar{H}_f^0$ for $\text{Na}^+(\text{aq})$



$$\Delta H_{\text{measured}} = +3.89 \text{ kJ}$$

$$+3.89 \text{ kJ} = -\Delta\bar{H}_f^0(\text{NaCl}(s)) + \Delta\bar{H}_f^0(\text{Na}^+(\text{aq})) + \Delta\bar{H}_f^0(\text{Cl}^-(\text{aq}))$$

$$+3.89 \text{ kJ} = -(-411.2 \text{ kJ}) + \Delta\bar{H}_f^0(\text{Na}^+(\text{aq})) + (-167.2 \text{ kJ})$$

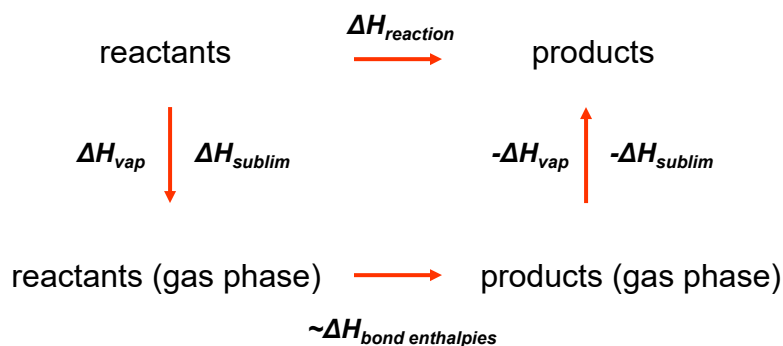
$$\Delta\bar{H}_f^0(\text{Na}^+(\text{aq})) = -240.1 \text{ kJ mol}^{-1}$$

| Substance | ΔH_f^\ddagger (kJ mol ⁻¹) | etc. |
|-----------------------------|---|------|
| $\text{Al}^{3+}(\text{aq})$ | -538.4 | |
| $\text{Ba}^{2+}(\text{aq})$ | -537.6 | |
| $\text{Br}^-(\text{aq})$ | -121.6 | |

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$\Delta H_{\text{reaction}}$ from bond enthalpies (p. 92)_{ER4th} [p. 69]_{ER3rd}



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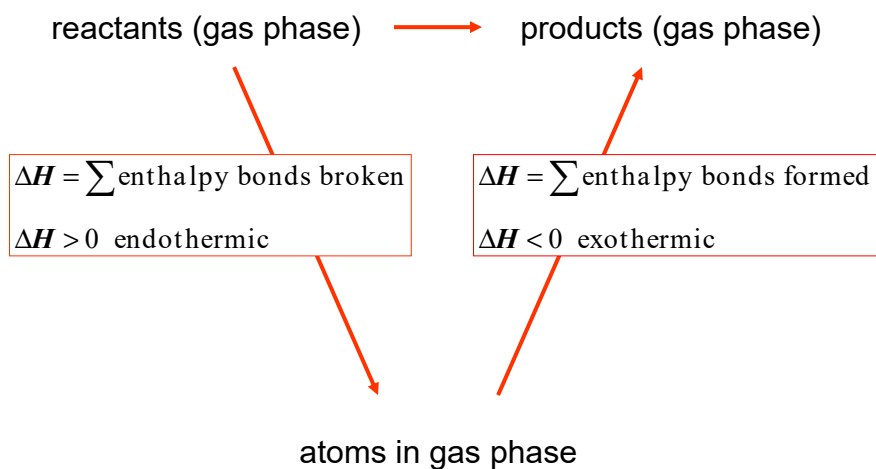
$\Delta H_{\text{reaction}}$ from bond enthalpies

- Similar bonds (C-H, C-C, C=C, C=O, etc) in similar molecule have similar enthalpies (energies)
- Use bond enthalpies (averaged over experimental data from several molecules) to approximate the enthalpies of the bonds broken in reactants and bonds formed in products to approximate **gas phase** $\Delta H_{\text{reaction}}$

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$\Delta H_{\text{reaction}}$ from bond enthalpies



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$\Delta H_{\text{reaction}}$ from bond enthalpies

TABLE 8.4 Average Bond Enthalpies (kJ/mol)

| Single Bonds | | | | | |
|--------------|-----|------|-----|-------|-----|
| C—H | 413 | N—H | 391 | O—H | 463 |
| C—C | 348 | N—N | 163 | O—O | 146 |
| C—N | 293 | N—O | 201 | O—F | 190 |
| C—O | 358 | N—F | 272 | O—Cl | 203 |
| C—F | 485 | N—Cl | 200 | O—I | 234 |
| C—Cl | 328 | N—Br | 243 | Br—F | 237 |
| C—Br | 276 | | | Br—Cl | 218 |
| C—I | 240 | H—H | 436 | S—H | 339 |
| C—S | 259 | H—F | 567 | S—F | 327 |
| | | H—Cl | 431 | S—Cl | 253 |
| | | H—Br | 366 | S—Br | 218 |
| | | H—I | 299 | S—S | 266 |
| Si—H | 323 | | | I—Cl | 208 |
| Si—Si | 226 | | | I—Br | 175 |
| Si—C | 301 | | | I—I | 151 |
| Si—O | 368 | | | | |

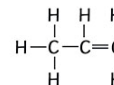
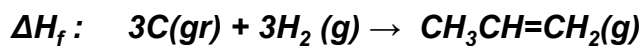
| Multiple Bonds | | | |
|----------------|------|----------------|-----|
| C=C | 614 | N=N | 418 |
| C≡C | 839 | N≡N | 941 |
| C=N | 615 | N=O | 607 |
| C≡N | 891 | | |
| C=O | 799 | O ₂ | 495 |
| C≡O | 1072 | S=O | 523 |
| | | S=S | 418 |

<http://wps.prenhall.com/wps/media/objects/165/169060/tool0801.gif>

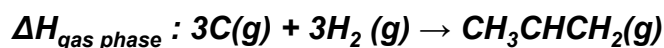
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example ΔH_f $\text{CH}_3\text{CH}=\text{CH}_2(\text{g})$

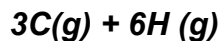


$$3\Delta \bar{H}_{\text{sub}}(\text{C}) = 3(717) \text{ kJ}$$



$$\Delta H = 3\text{BE}(\text{H}_2) = 3(436 \text{ kJ})$$

$$\Delta H = -6\text{BE}(\text{C-H}) - \text{BE}(\text{C-C}) - \text{BE}(\text{C=C}) = -6(413 \text{ kJ}) - (348 \text{ kJ}) - (614 \text{ kJ})$$



$$\Delta H_f = (3 \times 717 + 3 \times 436 - 6 \times 413 - 348 - 614) \text{ kJ} = 19 \text{ kJ}$$

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example ΔH_f $\text{CH}_3\text{CH}=\text{CH}_2(\text{g})$

$$\Delta H_f: 3\text{C}(\text{gr}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}=\text{CH}_2(\text{g})$$

\downarrow $3\Delta \bar{H}_{\text{sub}}(\text{C})=3(717) \text{ kJ}$

$$\Delta H_{\text{gas phase}}: 3\text{C}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}=\text{CH}_2(\text{g})$$

$\Delta H=3\text{BE}(\text{H}_2)$ $\Delta H=-6\text{BE}(\text{C-H})-\text{BE}(\text{C-C})-\text{BE}(\text{C}=\text{C})$

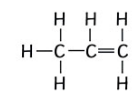


TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS

| Substance | Formula | Molecular Weight | ΔH_f° (kJ mol ⁻¹) |
|------------|-------------------------------|------------------|---|
| Propene(g) | C ₃ H ₆ | 42.08 | 20.0 |

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bond enthalpy vs bond energy

- often [mis]used interchangeably
Usually both meant to mean bond **enthalpy**
- bond **enthalpy**: thermodynamic heat measured at const P
- bond **energy**: the bond strength from quantum mechanical calculation
- can be interconverted by the $\Delta H = \Delta U + \Delta n_{\text{gas}}RT$ relation (p. 92 [68]_{3rd}; example problem 4.1 for O-H bond
bond energy = 461 kJ mol⁻¹ vs *bond enthalpy* = 463.5 kJ mol⁻¹)
- Table 4.3 E&R is weird (hard to read)

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table 4.3 E&R

| TABLE 4.3 MEAN BOND ENERGIES | | Selected Bond Energies (kJ/mol) | | | | | | | | | | | | | | | | |
|--|---|---------------------------------|----|----|----|----|----|--|--|--|--|--|--|--|--|--|--|----|
| 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 | | | | | | | | | | | |
| H, 2.20 432 — 432 459 565 | | | | | | | | | | | | | | | | | | He |
| Li, 0.69 105 — 243 — 573 | Be, 1.57 208 — — — 692 | | | | | | | | | | | | | | | | | Ne |
| Na, 0.99 72 — 197 — 477 | Mg, 1.91 149 — — — 513 | | | | | | | | | | | | | | | | | Ar |
| K, 0.82 40 — 180 — 490 | Sr, 1.00 195 — — — 550 | | | | | | | | | | | | | | | | | Kr |
| Rb, 0.82 45 — 163 — 490 | Sr, 0.95 84 — — — 653 | | | | | | | | | | | | | | | | | Xe |
| Cs, 0.70 44 — 178 — 502 | Ba, 0.89 84 — — — 561 576 | | | | | | | | | | | | | | | | | Rn |
| | | | | | | | | | | | | | | | | | | |

KEY

| | | |
|----------------|----------|-------------------------------|
| Element symbol | C, 2.55 | Electronegativity |
| C—C | 346 | Single bond with self |
| C=C | 612, 635 | Double, triple bond with self |
| C—H | 411 | Bond with H |
| C—O | 358, 399 | Single, double bond with O |
| C—F | 485 | Bond with F |

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$\Delta H_{\text{reaction}}$ from bond enthalpies

TABLE 8.4 Average Bond Enthalpies (kJ/mol)

| Single Bonds | | | | | |
|----------------|------|------|-----|----------------|-----|
| C—H | 413 | N—H | 391 | O—H | 463 |
| C—C | 348 | N—N | 163 | O—O | 146 |
| C—N | 293 | N—O | 201 | O—F | 190 |
| C—O | 358 | N—F | 272 | O—Cl | 203 |
| C—F | 485 | N—Cl | 200 | O—I | 234 |
| C—Cl | 328 | N—Br | 243 | | |
| C—Br | 276 | | | S—H | 339 |
| C—I | 240 | H—H | 436 | S—F | 327 |
| C—S | 259 | H—F | 567 | S—Cl | 253 |
| | | H—Cl | 431 | S—Br | 218 |
| Si—H | 323 | H—Br | 366 | S—S | 266 |
| Si—Si | 226 | H—I | 299 | | |
| Si—C | 301 | | | I—Cl | 208 |
| Si—O | 368 | | | I—Br | 175 |
| | | | | I—I | 151 |
| Multiple Bonds | | | | | |
| C=C | 614 | N=N | 418 | O ₂ | 495 |
| C≡C | 839 | N≡N | 941 | | |
| C=N | 615 | N=O | 607 | S=O | 523 |
| C≡N | 891 | | | S=S | 418 |
| C=O | 799 | | | | |
| C≡O | 1072 | | | | |

<http://wps.prenhall.com/wps/media/objects/165/169060/tool0801.gif>

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topics for thermochemistry, parts of Ch. 4 E&R

- ✓ • Calculate $\Delta H_{\text{reaction}}$
Hess's Law, standard heats of formation
- ✓ • $\Delta H_{\text{reaction}}$ vs $\Delta U_{\text{reaction}}$
- ✓ • Temperature (and pressure) dependence
of $\Delta H_{\text{reaction}}$
- ✓ • Calorimetry
- ✓ • Heats of solution
- ✓ • $\Delta H_{\text{reaction}}$ from bond enthalpies

----- MIDTERM 1 -----

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end of thermochemistry section !!!

on to the 2nd Law

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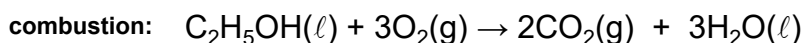
E&R_{4th} prob 4.33 HW3 #16

16. E&R_{4th} P4.33 If 4.206 g of ethanol, C₂H₅OH(l) is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 124.34 kJ.

a. Calculate $\Delta H^\circ_{\text{combustion}}$ for ethanol at 298.15 K.

b. Calculate ΔH°_f of ethanol at 298.15 K.

[for part b. use Appendix A (4.1) only; no peeking at A(4.2) !!]



a. $\Delta \bar{H}^0_{\text{combustion}}$

bomb calorimeter $\Rightarrow q_{??}$

measure convert to
 $q_v = \Delta \bar{U} \Rightarrow \Delta \bar{H}^0_{\text{combustion}}$

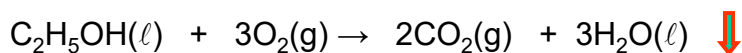
(assume pure liquids,

gases 1 bar partial pressure)

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E&R prob 4.33b HW3 #16 (cont) using ΔH^0_{comb} from 4.33a



$\Delta \bar{H}^0_f$: $\Delta \bar{H}^0_f(\text{EtOH})$ 0 -393.5 -285.8 kJ mol⁻¹

$\Delta H^0_{\text{comb}} = [(-1 \text{ mol})\Delta \bar{H}^0_f(\text{EtOH}) + (-3 \text{ mol})(0) + (2 \text{ mol})(-393.5 \frac{\text{kJ}}{\text{mol}}) + (3 \text{ mol})(-285.8 \frac{\text{kJ}}{\text{mol}})]$

$\sum_i \nu_i (\Delta \bar{H}^0_f)_i$ SOLVE FOR $\Delta H_f(\text{EtOH})$

$\Delta \bar{H}^0_f(\text{EtOH}) = [+ (2) (-393.5) + (3) (-285.8) - \Delta H^0_{\text{comb}}] \text{ kJ mol}^{-1}$

$\Delta \bar{H}^0_f(\text{EtOH}) = -279.7 \text{ kJ mol}^{-1}$ ↑

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Lectures 6-7 Thermochemistry

TABLE 4.1 (CONTINUED)

| Substance | ΔH_f° (kJ mol ⁻¹) | ΔG_f° (kJ mol ⁻¹) | S° (J mol ⁻¹ K ⁻¹) | $C_{p,m}$ (J mol ⁻¹ K ⁻¹) | Atomic or Molecular Weight (amu) |
|------------------------------------|--|--|--|--|----------------------------------|
| H(g) | 218.0 | 203.3 | 114.7 | 20.8 | 1.008 |
| OH(g) | 39.0 | 34.2 | 183.7 | 29.9 | 17.01 |
| H ₂ O(g) | -241.8 | -228.6 | 188.8 | 33.6 | 18.015 |
| H ₂ O(l) | <u>-285.8</u> | -237.1 | 70.0 | 75.3 | 18.015 |
| H ₂ O(s) | | | 48.0 | 36.2 (273 K) | 18.015 |
| H ₂ O ₂ (g) | -136.3 | -105.6 | 232.7 | 43.1 | 34.015 |
| H ⁺ (aq) | 0 | 0 | 0 | | 1.008 |
| OH ⁻ (aq) | -230.0 | -157.24 | -10.9 | | 17.01 |
| Carbon | | | | | |
| Graphite(s) | 0 | 0 | 5.74 | 8.52 | 12.011 |
| Diamond(s) | 1.89 | 2.90 | 2.38 | 6.12 | 12.011 |
| C(g) | 716.7 | 671.2 | 158.1 | 20.8 | 12.011 |
| CO(g) | -110.5 | -137.2 | 197.7 | 29.1 | 28.011 |
| CO ₂ (g) | <u>-393.5</u> | -394.4 | 213.8 | 37.1 | 44.010 |
| HCN(g) | 135.5 | 124.7 | 201.8 | 35.9 | 27.03 |
| CN ⁻ (aq) | 150.6 | 172.4 | 94.1 | | 26.02 |
| HCO ₃ ⁻ (aq) | -692.0 | -586.8 | 91.2 | | 61.02 |
| CO ₃ ²⁻ (aq) | -675.2 | -527.8 | -50.0 | | 60.01 |
| Oxygen | | | | | |
| O ₂ (g) | <u>0</u> | 0 | 205.2 | 29.4 | 31.999 |
| O(g) | 249.2 | 231.7 | 161.1 | 21.9 | 15.999 |
| O ₃ (g) | 142.7 | 163.2 | 238.9 | 39.2 | 47.998 |
| OH(g) | 39.0 | 34.22 | 183.7 | 29.9 | 17.01 |
| OH ⁻ (aq) | -230.0 | -157.2 | -10.9 | | 17.01 |

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E&R_{4th} prob 4.33b HW3 #16

16. E&R_{4th} P4.33 If 4.206 g of ethanol, C₂H₅OH(l) is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 124.34 kJ.

- Calculate $\Delta H^\circ_{\text{combustion}}$ for ethanol at 298.15 K.
- Calculate ΔH°_f of ethanol at 298.15 K.

[for part b. use Appendix A (4.1) only; no peeking at A(4.2) !!]

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Lectures 6-7 Thermochemistry

TABLE 4.1 (CONTINUED)

| Substance | ΔH_f° (kJ mol ⁻¹) | ΔG_f° (kJ mol ⁻¹) | S° (J mol ⁻¹ K ⁻¹) | $C_{p,m}^\circ$ (J mol ⁻¹ K ⁻¹) | Atomic or Molecular Weight (amu) |
|------------------------------------|--|--|--|--|----------------------------------|
| H(g) | 218.0 | 203.3 | 114.7 | 20.8 | 1.008 |
| OH(g) | 39.0 | 34.2 | 183.7 | 29.9 | 17.01 |
| H ₂ O(g) | -241.8 | -228.6 | 188.8 | 33.6 | 18.015 |
| H ₂ O(l) | <u>-285.8</u> | -237.1 | 70.0 | 75.3 | 18.015 |
| H ₂ O(s) | | | 48.0 | 36.2 (273 K) | 18.015 |
| H ₂ O ₂ (g) | -136.3 | -105.6 | 232.7 | 43.1 | 34.015 |
| H ⁺ (aq) | 0 | 0 | 0 | | 1.008 |
| OH ⁻ (aq) | -230.0 | -157.24 | -10.9 | | 17.01 |
| Carbon | | | | | |
| Graphite(s) | 0 | 0 | 5.74 | 8.52 | 12.011 |
| Diamond(s) | 1.89 | 2.90 | 2.38 | 6.12 | 12.011 |
| C(g) | 716.7 | 671.2 | 158.1 | 20.8 | 12.011 |
| CO(g) | -110.5 | -137.2 | 197.7 | 29.1 | 28.011 |
| CO ₂ (g) | <u>-393.5</u> | -394.4 | 213.8 | 37.1 | 44.010 |
| HCN(g) | 135.5 | 124.7 | 201.8 | 35.9 | 27.03 |
| CN ⁻ (aq) | 150.6 | 172.4 | 94.1 | | 26.02 |
| HCO ₃ ⁻ (aq) | -692.0 | -586.8 | 91.2 | | 61.02 |
| CO ₃ ²⁻ (aq) | -675.2 | -527.8 | -50.0 | | 60.01 |
| Oxygen | | | | | |
| O ₂ (g) | <u>0</u> | 0 | 205.2 | 29.4 | 31.999 |
| O(g) | 249.2 | 231.7 | 161.1 | 21.9 | 15.999 |
| O ₃ (g) | 142.7 | 163.2 | 238.9 | 39.2 | 47.998 |
| OH(g) | 39.0 | 34.22 | 183.7 | 29.9 | 17.01 |
| OH ⁻ (aq) | -230.0 | -157.2 | -10.9 | | 17.01 |

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TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS AT 298.15 K

| Substance | Formula | Molecular Weight | ΔH_f° (kJ mol ⁻¹) | ΔH_c° (kJ mol ⁻¹) | ΔG_f° (kJ mol ⁻¹) | S° (J mol ⁻¹ K ⁻¹) | $C_{p,m}^\circ$ (J mol ⁻¹ K ⁻¹) |
|-------------------|--|------------------|--|--|--|--|--|
| Carbon (graphite) | C | 12.011 | 0 | -393.5 | 0 | 5.74 | 8.52 |
| Carbon (diamond) | C | 12.011 | 1.89 | -395.4 | 2.90 | 2.38 | 6.12 |
| Carbon monoxide | CO | 28.01 | -110.5 | -283.0 | -137.2 | 197.7 | 29.1 |
| Acetone(l) | C ₃ H ₆ O | 58.08 | -248.4 | -1790 | -155.2 | 199.8 | 126.3 |
| Benzene(l) | <u>C₆H₆</u> | 78.12 | <u>49.1</u> | -3268 | 124.5 | 173.4 | <u>136.0</u> |
| Benzene(g) | C ₆ H ₆ | 78.12 | 82.9 | -3303 | 129.7 | 269.2 | 82.4 |
| Benzoic acid(s) | C ₇ H ₆ O ₂ | 122.13 | -385.2 | -3227 | -245.5 | 167.6 | 146.8 |
| 1,3-Butadiene(g) | C ₄ H ₆ | 54.09 | 110.0 | -2541 | | | 79.8 |
| Dimethyl ether(g) | C ₂ H ₆ O | 131.6 | -184.1 | -1460 | -112.6 | 266.4 | 64.4 |
| Ethane(g) | C ₂ H ₆ | 30.07 | -84.0 | -1561 | -32.0 | 229.2 | 52.5 |
| Ethanol(l) | C ₂ H ₆ O | 46.07 | -277.6 | -1367 | -174.8 | 160.7 | 112.3 |
| Ethanol(g) | C ₂ H ₆ O | 46.07 | -234.8 | -1367 | -167.9 | 281.6 | 65.6 |
| Ethene(g) | C ₂ H ₄ | 28.05 | 52.4 | -1411 | 68.4 | 219.3 | 42.9 |
| Ethyne(g) | <u>C₂H₂</u> | 26.04 | <u>227.4</u> | -1310 | 209.2 | 200.9 | <u>44.1</u> |
| Formaldehyde(g) | CH ₂ O | 30.03 | -108.6 | -571 | -102.5 | 218.8 | 35.4 |

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standard states and standard heats of formation

| | | |
|---------------------|-----------------|----------------------------------|
| standard state (°): | gas | partial pressure 1 bar |
| | liquid or solid | pure substance at 1 bar |
| | solute in soln | 1 M (molar) [\sim 1m (molal)] |



standard molar heat of formation (\bar{H}_f° or $\Delta \bar{H}_f^\circ$):
 $(\Delta H_T^\circ)_{\text{reaction}}$ where 1 mole of substance is produced from
elements in their most stable form at given temperature
(some texts, e.g. E&R_{4th}, say $T=298^\circ$ also part of definition)

$\Delta \bar{H}_f^\circ$ at 298K in kJ/mol

C(gr)=0 O₂(g)=0 C(dia)=1.89 H₂O(g)=-241.8 H₂O(l)=-285.8

F₂(g)=0 Cl₂(g)=0 I₂(g)=62.4 I₂(s)=0



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