

Chemistry 163B

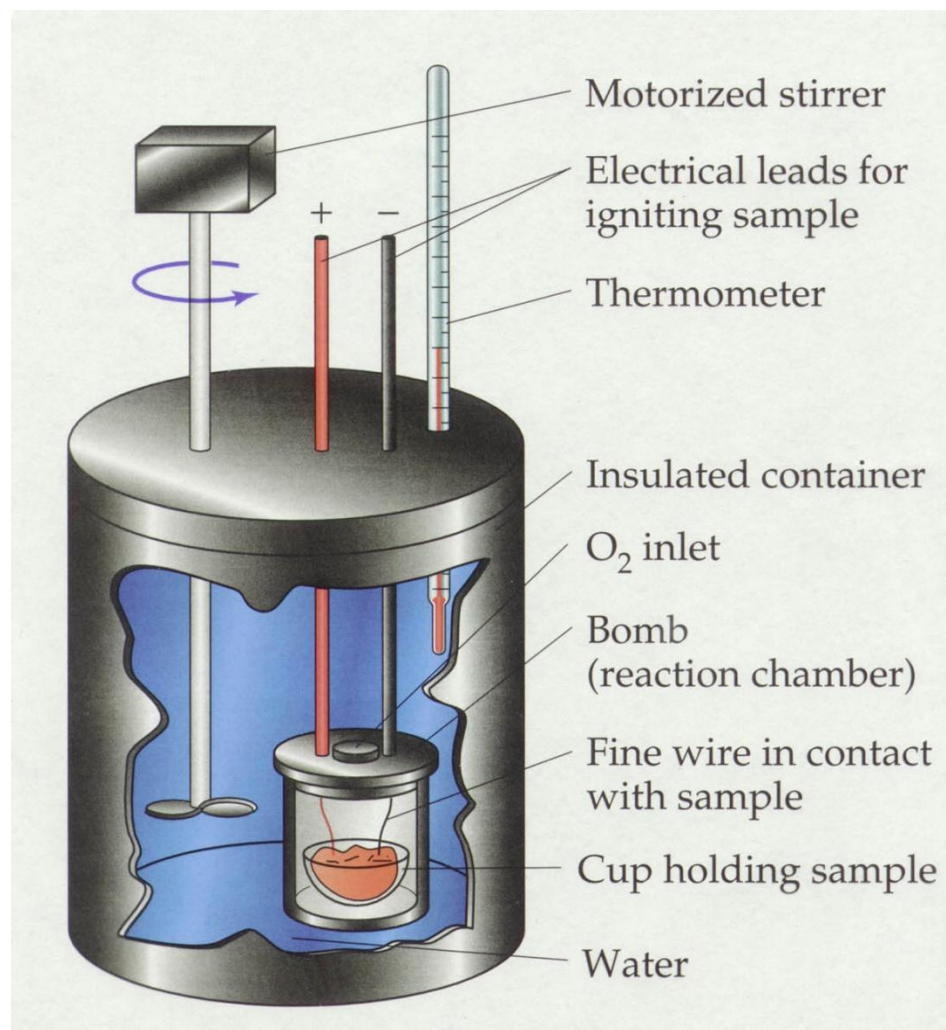
Thermochemistry

Chapter 4 Engel & Reid

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

$$\Delta U_V = q_V$$

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



## heats of reactions (constant volume; fig 4.3 E&R)

$$\Delta U_V = q_V$$

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

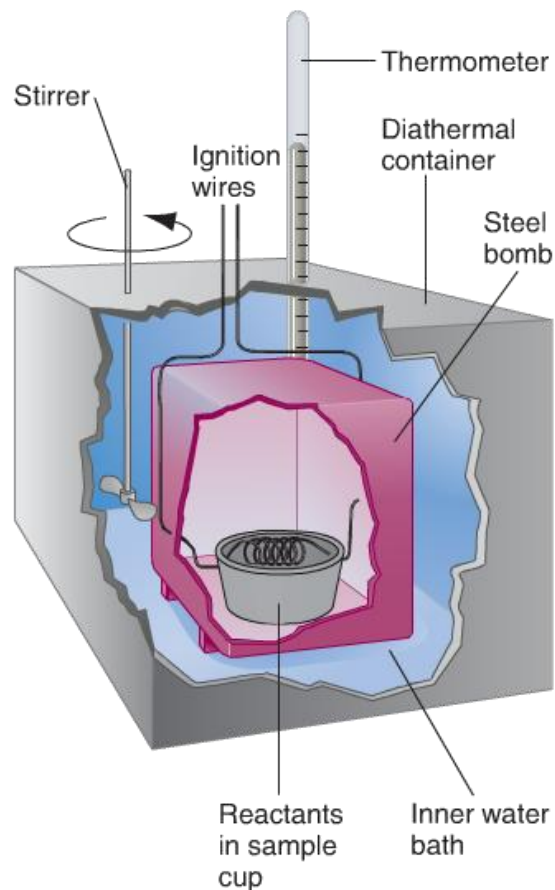


FIGURE 4.3

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 O<sub>2</sub> 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.

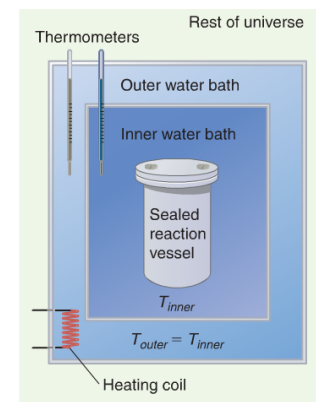


FIGURE 2.3

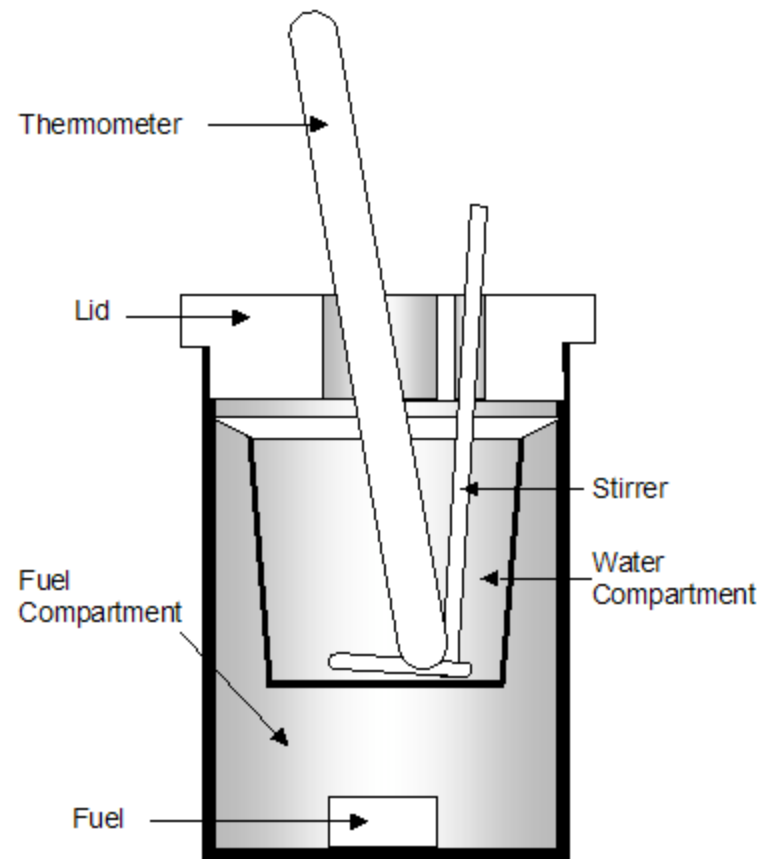
An isolated composite system is created in which the surroundings to the system of interest are limited in extent. The walls surrounding the inner water bath are rigid.

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

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$$\Delta H_P = q_P$$

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

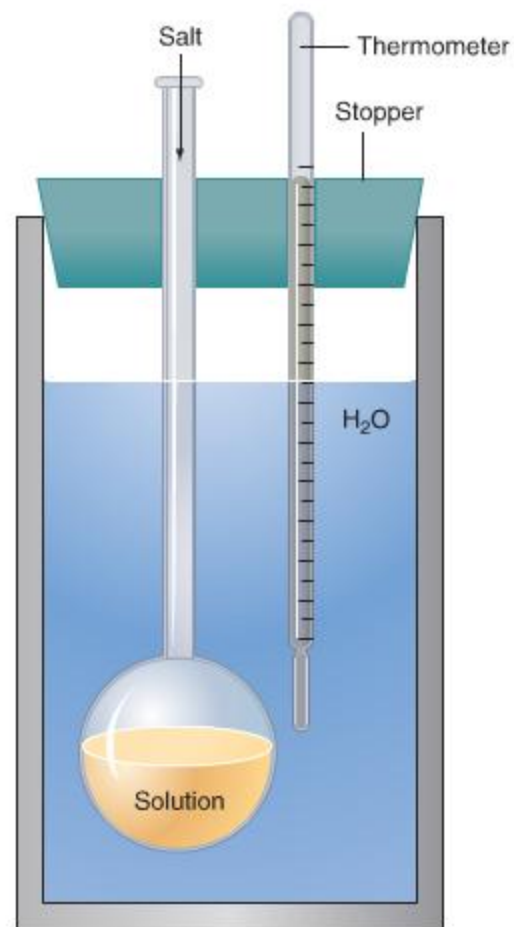


## heats of reactions (constant pressure; fig 4.4 E&R)

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$$\Delta H_P = q_P$$

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

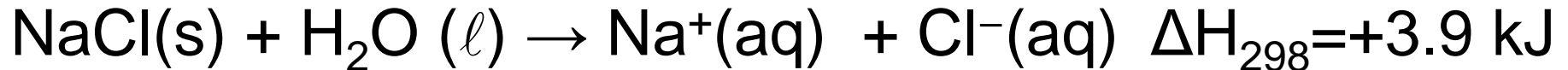
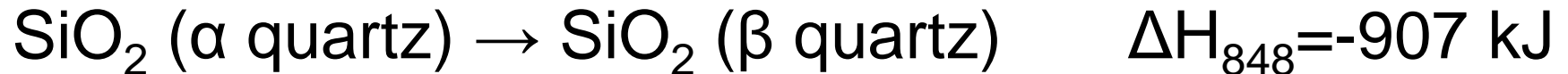
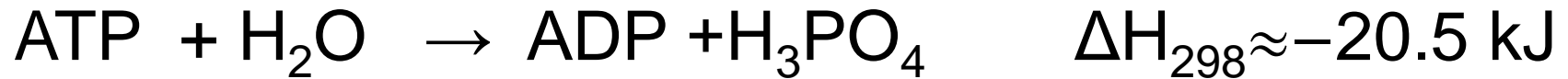
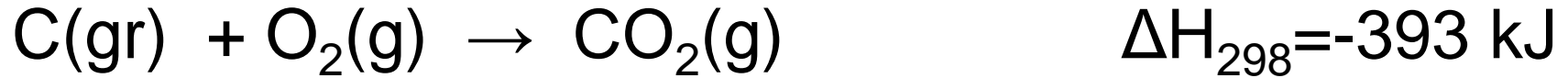


**FIGURE 4.4**

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

*most reactions at P constant,  $\Delta H_P = q_P$*

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

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HW#3 16

HW#4 17,18

- Calculate  $\Delta H_{\text{reaction}}$   
Hess's Law, standard heats of formation

HW#3 16

- $\Delta H_{\text{reaction}}$  vs  $\Delta U_{\text{reaction}}$

HW#4 18, \*19

- Temperature (*and later* pressure) dependence of  $\Delta H_{\text{reaction}}$

- Calorimetry

- Heats of solution

HW#4

20, 21

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

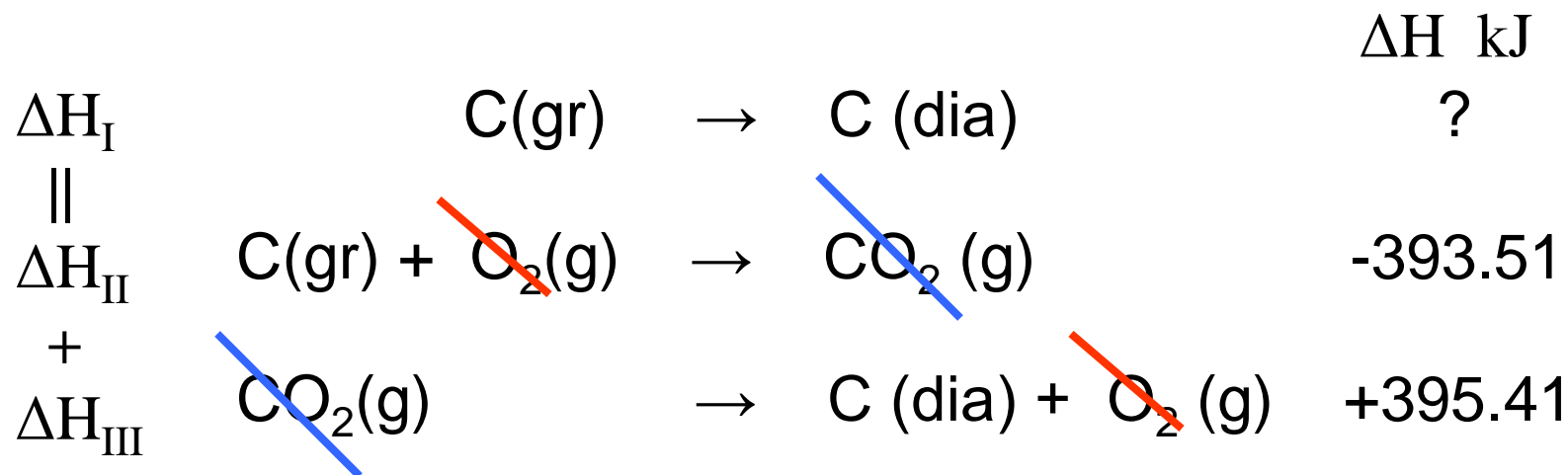
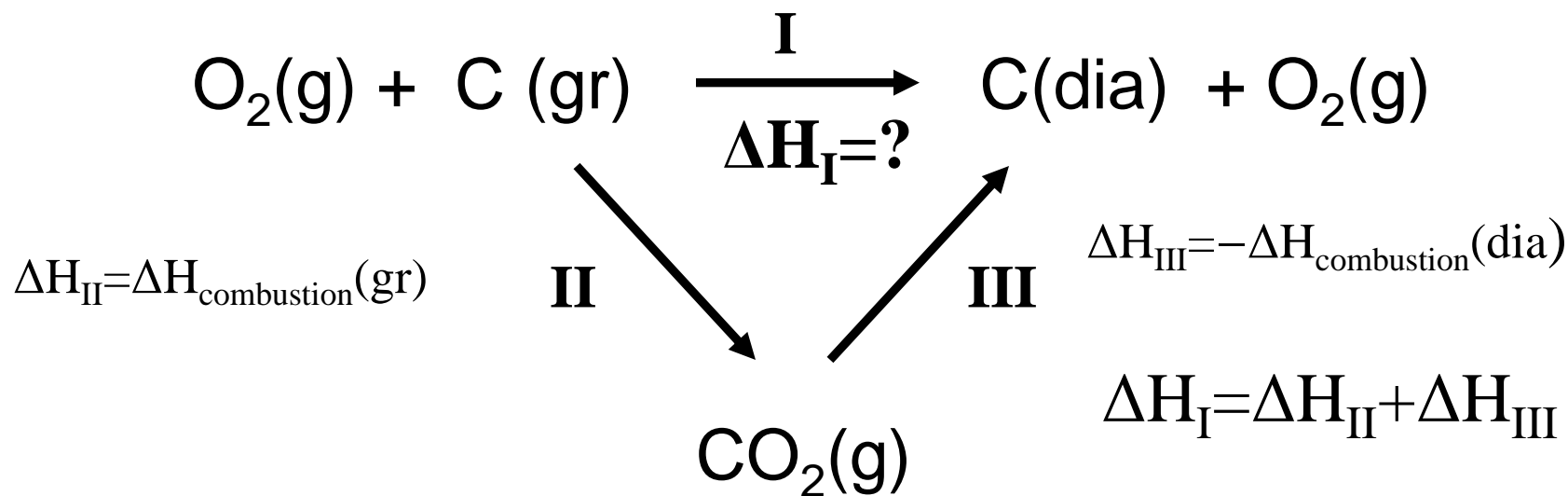
## Hess's Law

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



## $\Delta H$ State Function $\Rightarrow$ Hess's Law



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

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

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- stoichiometry  
 *$\Delta H$  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

*notation:  $\Delta H$  (etc) in terms of molar enthalpies and stoichiometric coefficients*

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

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

total enthalpy of reactants

molar enthalpy of reactant  $i$

number of moles of  $i$   
in stoichiometry

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

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

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

$v_i = n_i$  if  $i$  is product species

$v_i = -n_i$  if  $i$  is reactant species

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

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$$H \equiv U + PV$$

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

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

assume:

i)  $PV$  and  $\Delta PV$  is small for solids and liquids

ii) Gasses follow ideal gas law

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

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

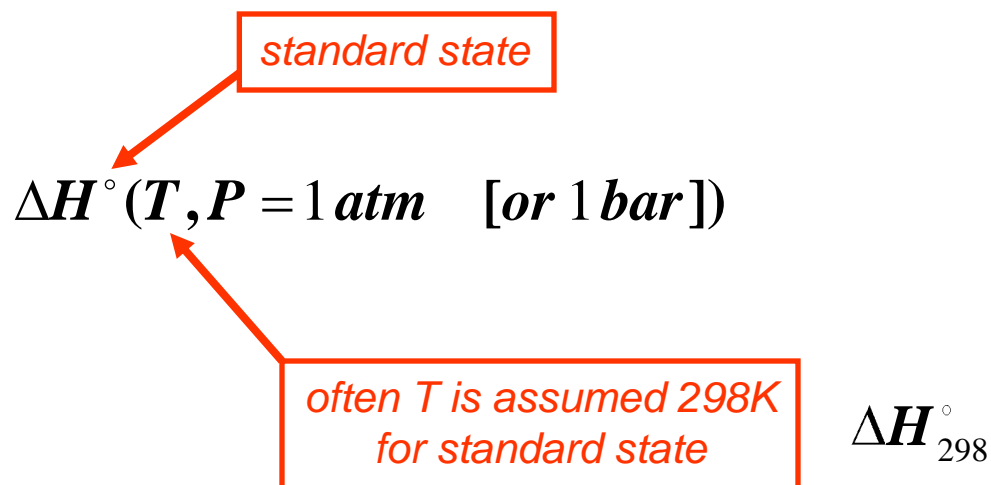
$$\Delta PV = \Delta n_{\text{gas}} RT$$

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

E&R eqn 4.25

# standard states and enthalpies of formation

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define standard states



$$(\Delta \bar{H}^\circ_{298})_{\text{formation}} \equiv \bar{H}^\circ_f$$

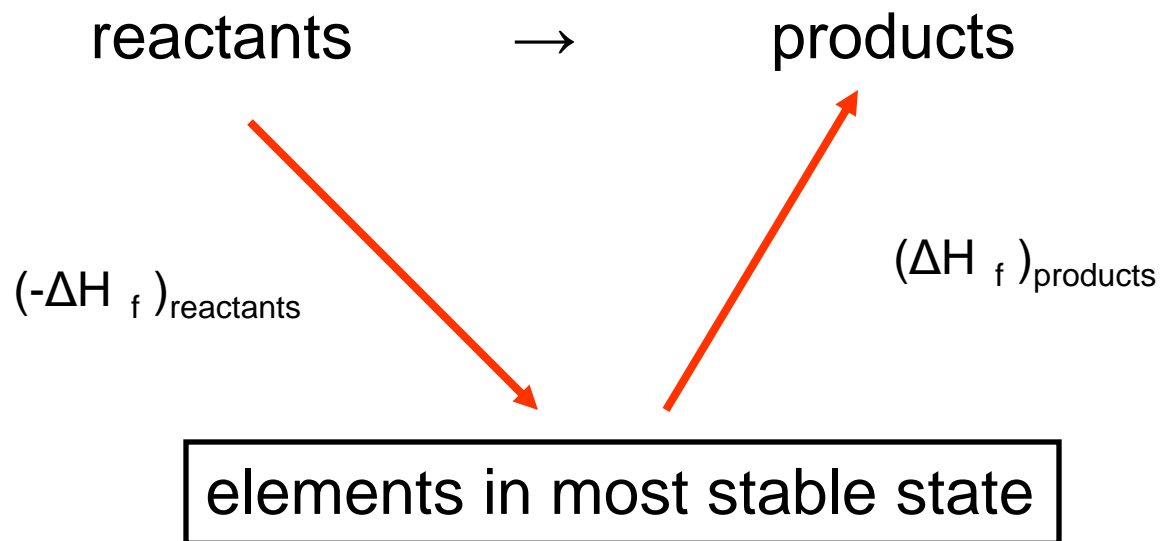
molar enthalpy of formation

define enthalpy of formation



# $\Delta H_{rxn}$ from $H_f$

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

do HW#3 problem 16b (E&R 4.20b)



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

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- ✓ • 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 -----

## temperature dependence of $H$ of substance at constant $P$

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

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

$T_1 \rightarrow T_2$



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

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

$$\Delta H_{\text{rxn}} \quad T_1, P$$

VS

$$\Delta H_{\text{rxn}} \quad T_2, P$$

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

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

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

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

change of  $\Delta H_{\text{rxn}}$   
 $T_1 \rightarrow T_2$

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

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

example problems :  $\Delta H$  from  $H_f$  and  $\Delta H$   $T=298K \rightarrow 398K$

$$\begin{array}{l}
 \Delta \bar{H}_f^\circ \quad 298^\circ \quad 227.4 \quad 49.1 \quad \text{calc } \Delta H^\circ_{298} \quad \text{kJ mol}^{-1} \\
 \Delta H^\circ_{298^\circ} \quad -3(227.4) + 1(49.1) = -633.1 \text{ kJ} \quad \text{[per mol } C_6H_6(l)\text{]} \\
 \text{[ (mol) (kJ mol}^{-1}\text{) + (mol)(kJ mol}^{-1}\text{) = kJ}
 \end{array}$$



$$\begin{array}{l}
 \bar{C}_P \quad 44. \quad 136.0 \quad \text{calc } \Delta H^\circ_{398} \quad \text{(J K}^{-1}\text{ mol}^{-1}\text{)} \\
 \Delta \bar{C}_P \quad -3(44.0) \quad + \quad 1(136.0) \quad = 4.0 \text{ (J K}^{-1}\text{)}
 \end{array}$$



$$(\Delta H^\circ)_{398^\circ} = (\Delta H^\circ)_{298^\circ} + \int_{298}^{398} \Delta C_P dT = (\Delta H^\circ)_{298^\circ} + \Delta C_P \Delta T \quad \text{[ } C_P \text{ independent of } T \text{]}$$

$$(\Delta H^\circ)_{398^\circ} = -633.1 \text{ kJ} + (4.0 \times 10^{-3} \text{ kJ K}^{-1})(100\text{K}) = -632.7 \text{ kJ}$$

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

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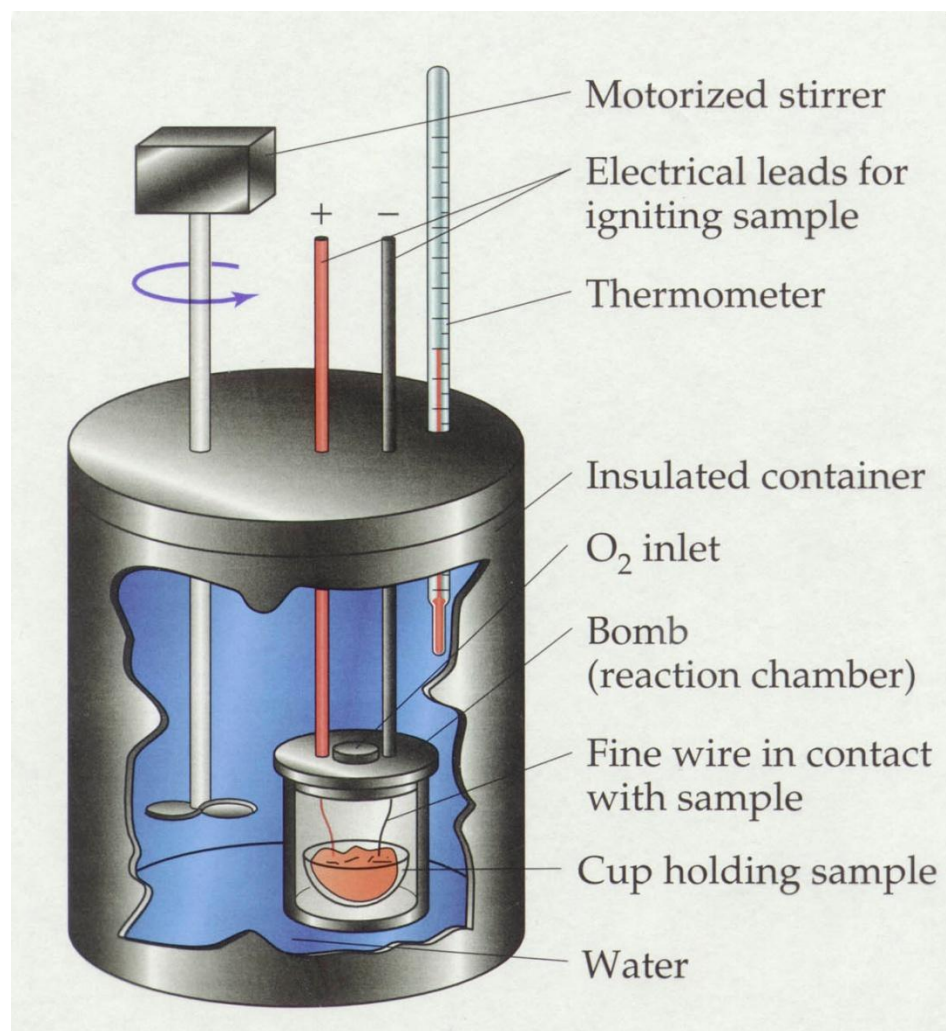
- ✓ • Calculate  $\Delta H_{\text{reaction}}$   
Hess's Law, standard heats of formation
- ✓ •  $\Delta H_{\text{reaction}}$  vs  $\Delta U_{\text{reaction}}$
- ✓ • Temperature (and pressure) dependence  
of  $\Delta H_{\text{reaction}}$ 
  - Calorimetry
  - Heats of solution
  - $\Delta H_{\text{reaction}}$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

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

## heats of reactions (constant volume)

$$\Delta U_V = q_V$$

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

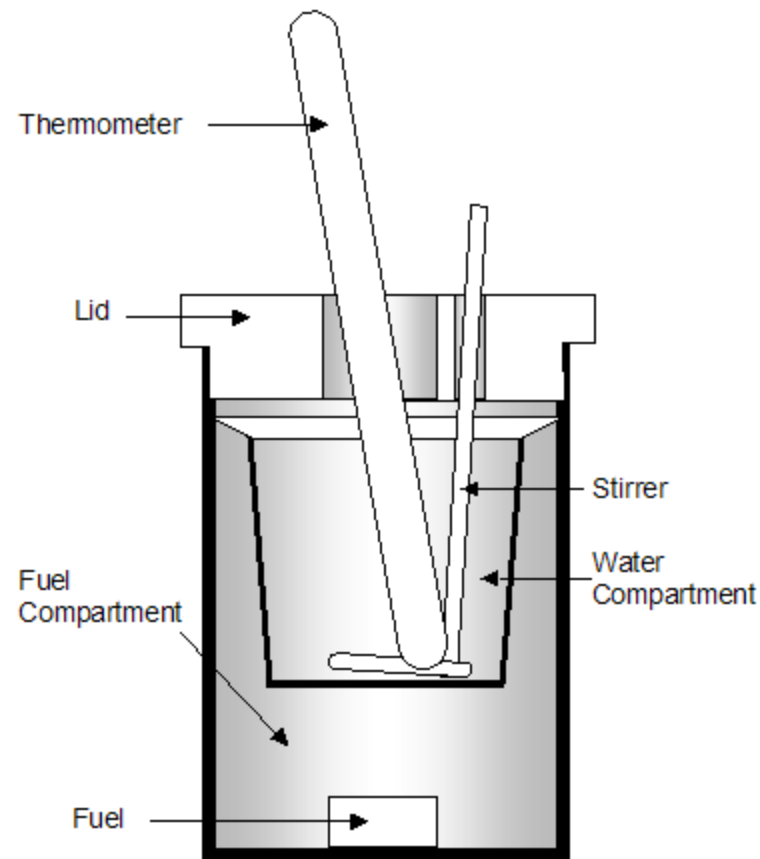


## heats of reactions (constant pressure)

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$$\Delta H_P = q_P$$

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



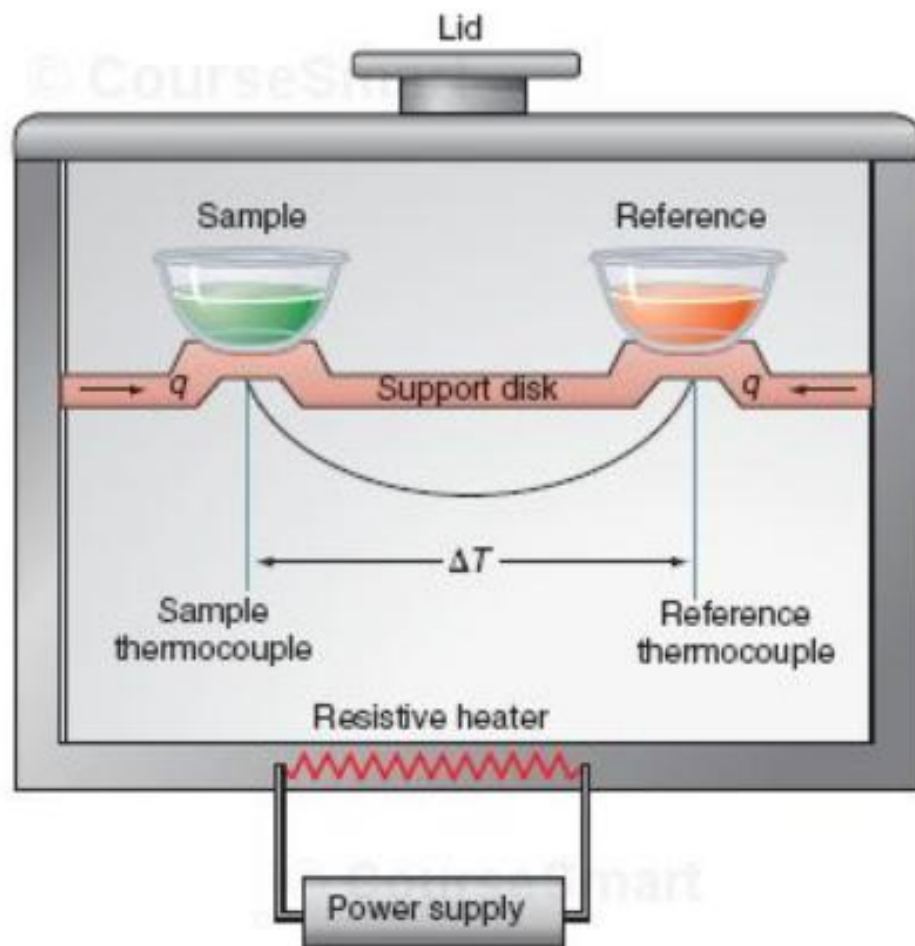
## *DSC- differential scanning calorimetry (enrichment, don't FRET)*

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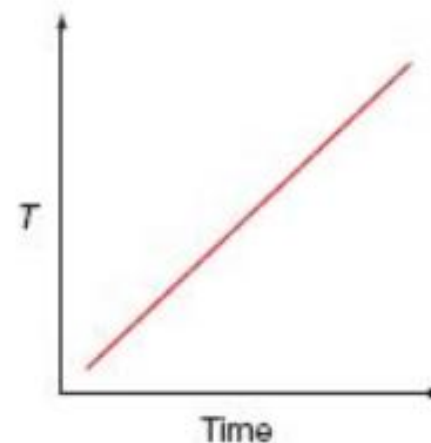


useful for small samples (often biological)

*DTA differential thermal analysis*  
*DSC differential scanning calorimetry*



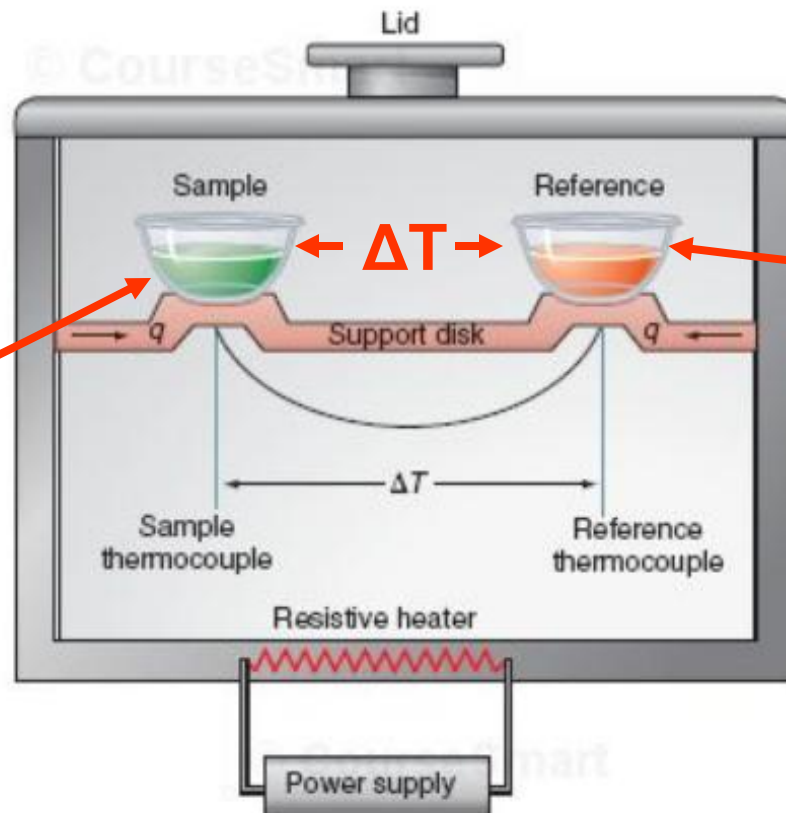
heat input



T of reference rises linearly with time

*DTA differential thermal analysis*  
*DSC differential scanning calorimetry*

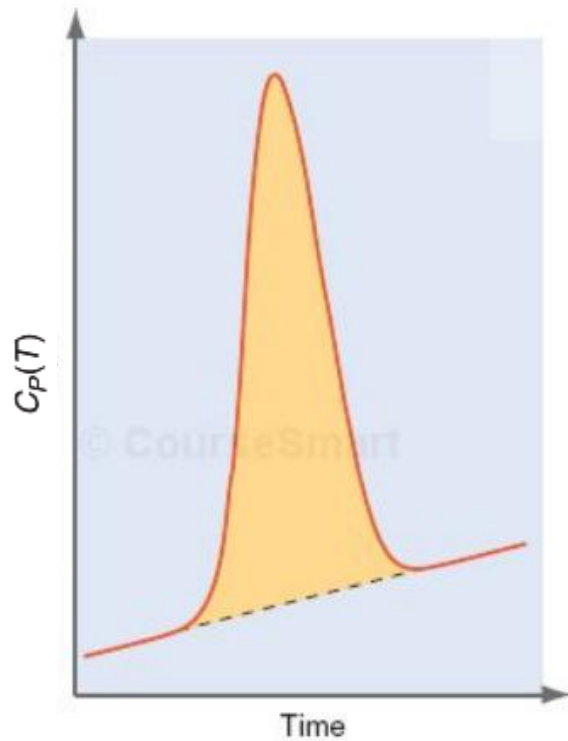
T rise due to  $q$  from calorimeter into sample  
**PLUS**  
 $\Delta H$  from process (e.g. chemical reaction, phase change or protein denaturation)



T rise due to  $q$  from calorimeter into reference



## denaturation of protein



$C_{p\text{sample}}$  increases during denaturation since some of  $q_{\text{in}}$  goes to denaturation

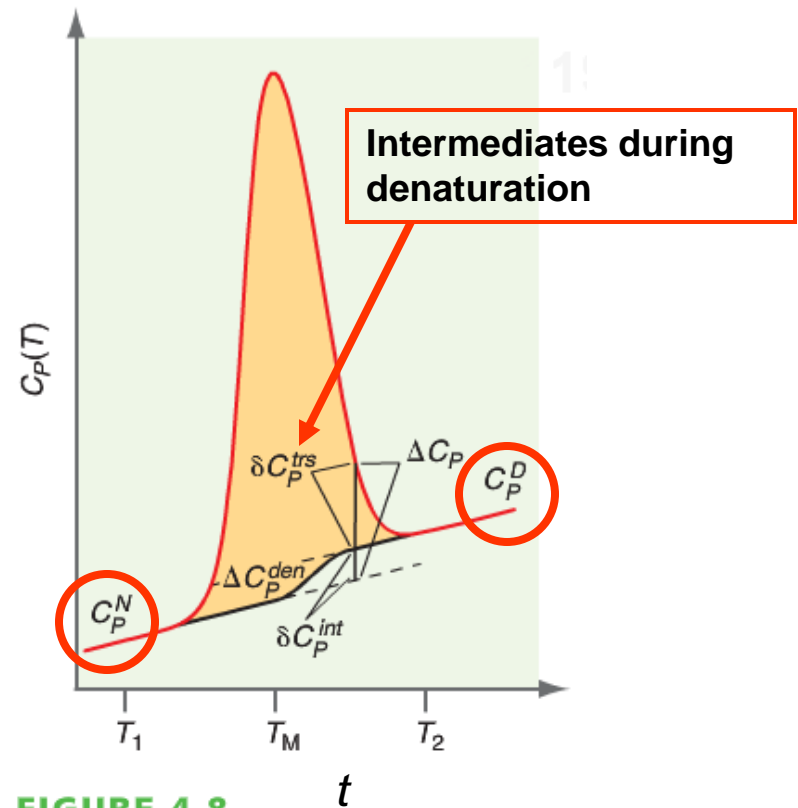


FIGURE 4.8

## how $H$ and $\Delta H$ change with pressure (don't FRET now)

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will prove later:

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

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

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

Will show later:

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

*heats of formation of ions (heat of solutions), Example 4.4 p 73*

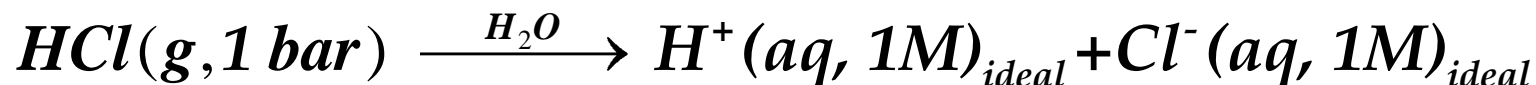
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importance: how to assign  $\bar{H}_f^0$  for an individual ion in solution  
since ions come in 'pairs'

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  $\text{H}^+$

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



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

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

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

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

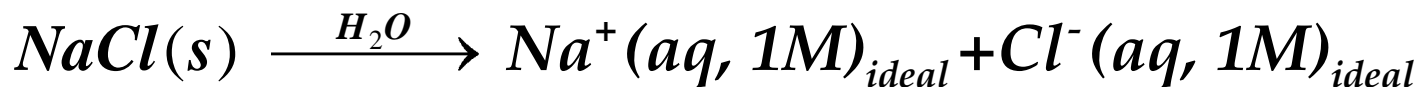
GOT  $\bar{H}_f^0$  for  $Cl^-(aq)$

NOW

## heats of formation of ions (heat of solutions)

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



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

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

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

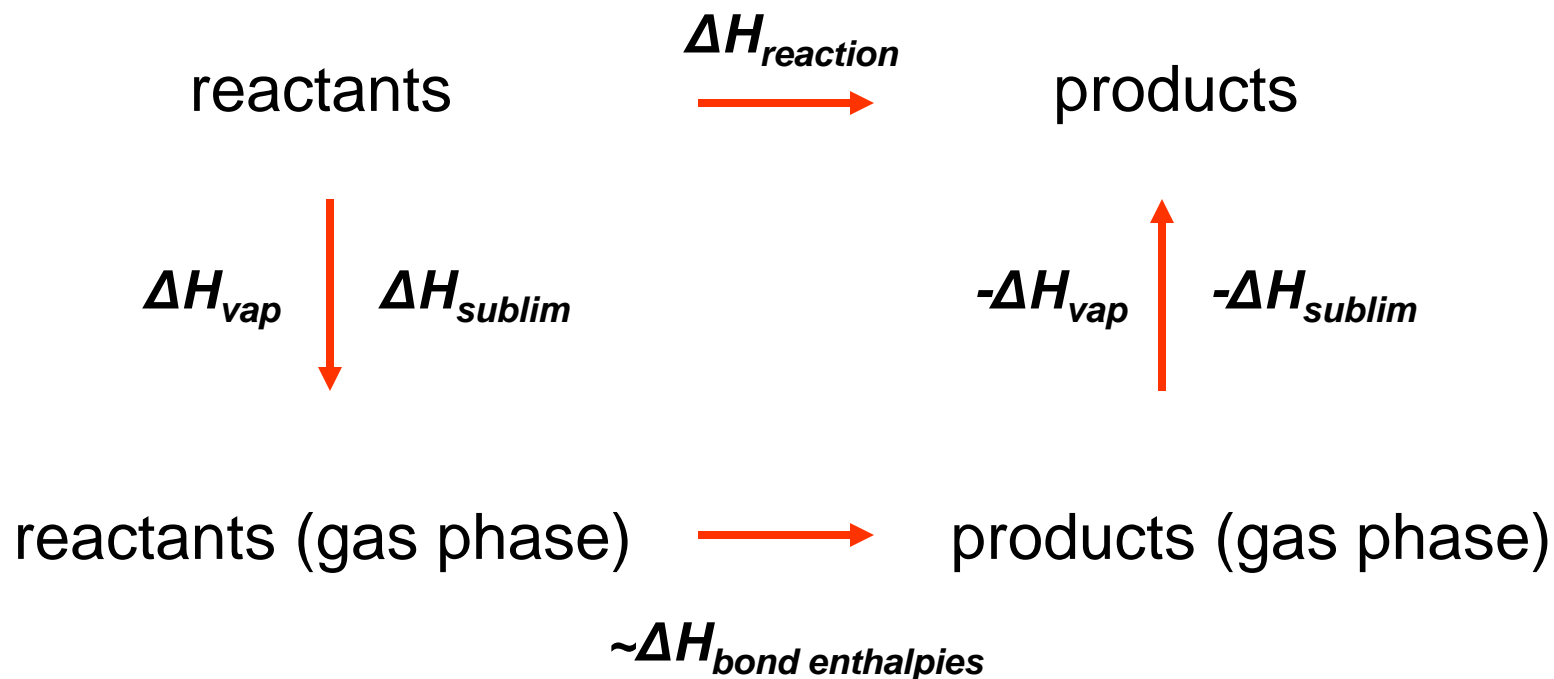
$$\bar{H}_f^0(Na^+(aq)) = -240.1 \text{ kJ mol}^{-1}$$

Substance	$\Delta H_f^0$ (kJ mol <sup>-1</sup> )
$Al^{3+}(aq)$	-538.4
$Ba^{2+}(aq)$	-537.6
$Br^-(aq)$	-121.6

etc.

# $\Delta H_{\text{reaction}}$ from bond enthalpies (p. 69)

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

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- 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**  $\Delta H_{\text{reaction}}$

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

---

reactants (gas phase)  $\longrightarrow$  products (gas phase)

$\Delta H = \sum \text{enthalpy bonds broken}$

$\Delta H > 0$  *endothermic*

$\Delta H = \sum \text{enthalpy bonds formed}$

$\Delta H < 0$  *exothermic*

atoms in gas phase



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

**TABLE 8.4 Average Bond Enthalpies (kJ/mol)**

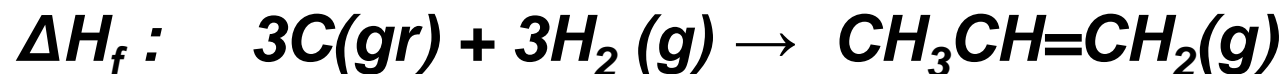
**Single Bonds**

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

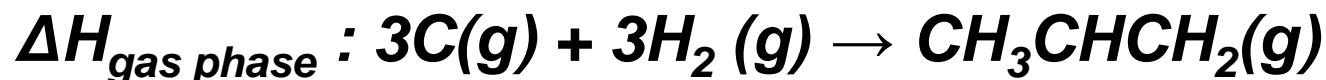
**Multiple Bonds**

C=C	614	N=N	418	O <sub>2</sub>	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				

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



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



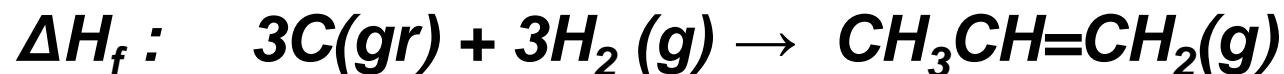
$$\Delta H = 3\text{BE}(\text{H}_2) \\ = 3(436 \text{ kJ})$$

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

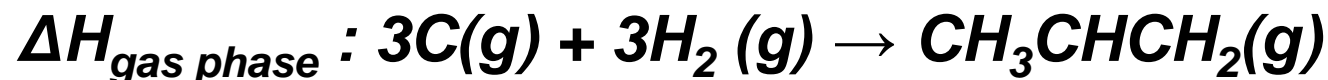


$$\Delta H_f = (3 \times 717 + 3 \times 436 - 6 \times 413 - 348 - 614) \text{ kJ} = 19 \text{ kJ}$$

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



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



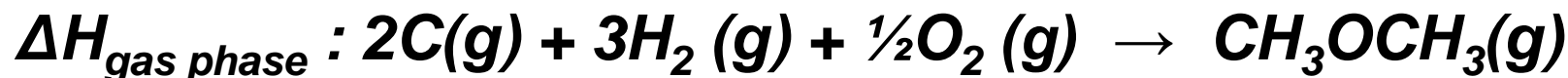
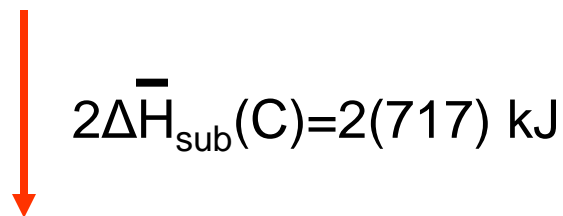
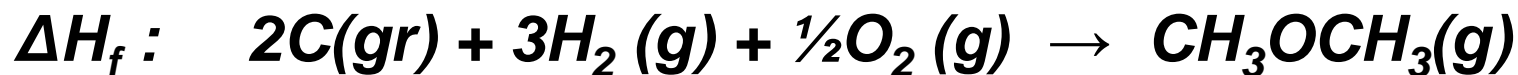
$$\Delta H = 3\text{BE}(\text{H}_2)$$

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

TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS

Substance	Formula	Molecular Weight	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
Propene(g)	C <sub>3</sub> H <sub>6</sub>	42.08	20.0

example  $\Delta H_f$   $\text{CH}_3\text{OCH}_3(\text{g})$

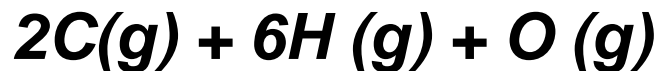


$$\Delta H = 3\text{BE}(\text{H}_2) + \frac{1}{2}\text{BE}(\text{O}_2)$$

$$= 3(436\text{kJ}) + \frac{1}{2}(495\text{kJ})$$

$$\Delta H = -6\text{BE}(\text{C-H}) - 2\text{BE}(\text{C-O})$$

$$= -6(413\text{kJ}) - 2(358\text{kJ})$$



$$\Delta H_f = (2 \times 717 + 3 \times 436 + \frac{1}{2} \times 495 - 6 \times 413 - 2 \times 358) \text{ kJ} = -204 \text{ kJ}$$

Substance	Formula	Molecular Weight	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
Dimethyl ether(g)	C <sub>2</sub> H <sub>6</sub> O	131.6	-184.1

## *bond enthalpy vs bond energy*

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- 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. 68; example problem 4.1 for O-H bond  
*bond energy = 461 kJ mol<sup>-1</sup> vs bond enthalpy = 463.5 kJ mol<sup>-1</sup>*)
- Table 4.3 E&R is weird (hard to read)

# table 4.3 E&R

**TABLE 4.3 MEAN BOND ENERGIES**

1	2	Selected Bond Energies (kJ/mol)						13	14	15	16	17	18
H, 2.20 432 — 432 459 565													He
Li, 0.98 105 — 243 — 573	Be, 1.57 208 — — 444 632						B, 2.04 293 — 389 536,636 613	C, 2.55 346 602,835 411 358,799 485	N, 3.04 167 418,942 386 201,607 283	O, 3.44 142 494 386 142,494 190	F, 3.98 155 — 565 — 155		Ne
Na, 0.93 72 — 197 — 477	Mg, 1.31 129 — — 377 513						Al, 1.61 — — 272 — 583	Si, 1.90 222 318 318 452,640 565	P, 2.10 —220 —481 322 335,544 490	S, 2.59 240 240 363 —,523 284	Cl, 3.16 240 — 428 218 249		Ar
K, 0.82 49 — 180 — 490	Sr, 1.00 105 — — 460 550						Ga, 1.81 113 — — — 469	Ge, 2.01 188 272 — — 470	As, 2.18 146 —360 247 301,389 440	Se, 2.55 172 272 276 — 351	Br, 2.96 190 — 362 201 250		Kr
Rb, 0.82 45 — 163 — 490	Sr, 0.95 84 — — 347 553						In, 1.78 100 — — — 523	Sn, 1.80 146 — — — 450	Sb, 2.05 121 —295 — — 420	Te, 2.10 126 218 238 — 393	I, 2.66 149 — 295 201 278		Xe
Cs, 0.79 44 — 176 — 502	Ba, 0.89 44 — — 467,561 578						Tl, 2.04 — — — — 439	Pb, 2.33 — — — — 360	Bi, 2.02 — —,192 — — 350	Po, 2.00 — — — — —	At, 2.20 116 — — — —		Rn

**KEY**

Element symbol	C, 2.55	Electronegativity
C—C	346	Single bond with self
C=C, C≡C	602,835	Double, triple bond with self
H—C	411	Bond with H
O—C, O=C	358,799	Single, double bond with O
C—F	485	Bond with F

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

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- ✓ • 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 -----

*end of thermochemistry section !!!*

*on to the 2<sup>nd</sup> Law*

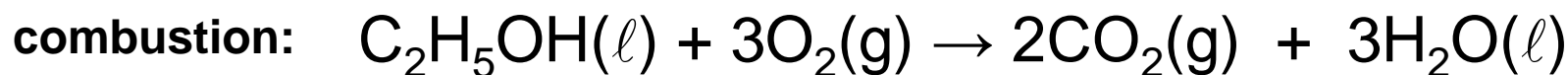


**P4.20** If 3.365 g of ethanol  $\text{C}_2\text{H}_5\text{OH}(\ell)$  is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 99.472 kJ.

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

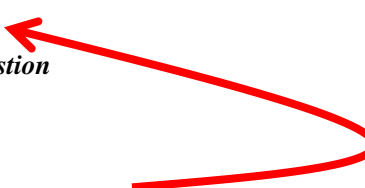
b. Calculate  $\Delta H_f^\circ$  of ethanol at 298.15 K.

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



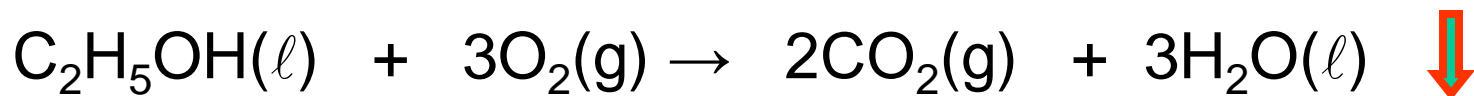
a.  $\Delta \bar{H}_{\text{combustion}}^0$

*bomb calorimeter*  $\Rightarrow q_{??}$

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


*(assume pure liquids,*

*gases 1 bar partial pressure)*



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

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

SOLVE FOR  $H_f(\text{EtOH})$

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

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



**TABLE 4.1 (CONTINUED)**

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	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 <sub>2</sub> O(g)	-241.8	-228.6	188.8	33.6	18.015
H <sub>2</sub> O(l)	<u>-285.8</u>	-237.1	70.0	75.3	18.015
H <sub>2</sub> O(s)			48.0	36.2 (273 K)	18.015
H <sub>2</sub> O <sub>2</sub> (g)	-136.3	-105.6	232.7	43.1	34.015
H <sup>+</sup> (aq)	0	0	0		1.008
OH <sup>-</sup> (aq)	-230.0	-157.24	-10.9		17.01
<b>Carbon</b>					
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 <sub>2</sub> (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 <sup>-</sup> (aq)	150.6	172.4	94.1		26.02
HCO <sub>3</sub> <sup>-</sup> (aq)	-692.0	-586.8	91.2		61.02
CO <sub>3</sub> <sup>2-</sup> (aq)	-675.2	-527.8	-50.0		60.01
<b>Oxygen</b>					
O <sub>2</sub> (g)	<u>0</u>	0	205.2	29.4	31.999
O(g)	249.2	231.7	161.1	21.9	15.999
O <sub>3</sub> (g)	142.7	163.2	238.9	39.2	47.998
OH(g)	39.0	34.22	183.7	29.9	17.01
OH <sup>-</sup> (aq)	-230.0	-157.2	-10.9		17.01



**P4.20** If 3.059 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$  is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 90.447 kJ.

- a. Calculate  $\Delta H_{\text{combustion}}^\circ$  for ethanol at 298.15 K.
- b. Calculate  $\Delta H_f^\circ$  of ethanol at 298.15 K.

**TABLE 4.1 (CONTINUED)**

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	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 <sub>2</sub> O(g)	-241.8	-228.6	188.8	33.6	18.015
H <sub>2</sub> O(l)	<u>-285.8</u>	-237.1	70.0	75.3	18.015
H <sub>2</sub> O(s)			48.0	36.2 (273 K)	18.015
H <sub>2</sub> O <sub>2</sub> (g)	-136.3	-105.6	232.7	43.1	34.015
H <sup>+</sup> (aq)	0	0	0		1.008
OH <sup>-</sup> (aq)	-230.0	-157.24	-10.9		17.01
<b>Carbon</b>					
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 <sub>2</sub> (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 <sup>-</sup> (aq)	150.6	172.4	94.1		26.02
HCO <sub>3</sub> <sup>-</sup> (aq)	-692.0	-586.8	91.2		61.02
CO <sub>3</sub> <sup>2-</sup> (aq)	-675.2	-527.8	-50.0		60.01
<b>Oxygen</b>					
O <sub>2</sub> (g)	<u>0</u>	0	205.2	29.4	31.999
O(g)	249.2	231.7	161.1	21.9	15.999
O <sub>3</sub> (g)	142.7	163.2	238.9	39.2	47.998
OH(g)	39.0	34.22	183.7	29.9	17.01
OH <sup>-</sup> (aq)	-230.0	-157.2	-10.9		17.01



**TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS AT 298.15 K**

Substance	Formula	Molecular Weight	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H_{combustion}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
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 <sub>3</sub> H <sub>6</sub> O	58.08	-248.4	-1790	-155.2	199.8	126.3
Benzene(l)	<u>C<sub>6</sub>H<sub>6</sub></u>	78.12	<u>49.1</u>	-3268	124.5	173.4	<u>136.0</u>
Benzene(g)	C <sub>6</sub> H <sub>6</sub>	78.12	82.9	-3303	129.7	269.2	82.4
Benzoic acid(s)	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122.13	-385.2	-3227	-245.5	167.6	146.8
1,3-Butadiene(g)	C <sub>4</sub> H <sub>6</sub>	54.09	110.0	-2541			79.8
Dimethyl ether(g)	C <sub>2</sub> H <sub>6</sub> O	131.6	-184.1	-1460	-112.6	266.4	64.4
Ethane(g)	C <sub>2</sub> H <sub>6</sub>	30.07	-84.0	-1561	-32.0	229.2	52.5
Ethanol(l)	C <sub>2</sub> H <sub>6</sub> O	46.07	-277.6	-1367	-174.8	160.7	112.3
Ethanol(g)	C <sub>2</sub> H <sub>6</sub> O	46.07	-234.8	-1367	-167.9	281.6	65.6
Ethene(g)	C <sub>2</sub> H <sub>4</sub>	28.05	52.4	-1411	68.4	219.3	42.9
Ethyne(g)	<u>C<sub>2</sub>H<sub>2</sub></u>	26.04	<u>227.4</u>	-1310	209.2	200.9	<u>44</u>
Formaldehyde(g)	CH <sub>2</sub> O	30.03	-108.6	-571	-102.5	218.8	35.4



## standard states and standard heats of formation

---

standard state ( $^{\circ}$ ):	gas	partial pressure 1 bar
	liquid or solid	pure substance at 1 bar
	solute in soln	1 M



standard molar heat of formation ( $H_f^{\circ}$ ):  
 $(\Delta H_T^{\circ})_{\text{reaction}}$  where 1 mole of substance is produced  
from **elements in their most stable form at given  
temperature**

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

$C(\text{gr})=0$   $O_2(\text{g})=0$   $C(\text{dia})=1.89$   $H_2O(\text{g})=-241.8$   $H_2O(\ell)=-285.8$   
 $F_2(\text{g})=0$   $Cl_2(\text{g})=0$   $I_2(\text{g})=62.4$   $I_2(\text{s})=0$



# Raff Table 3.2 bond enthalpies

**Table 3.2** Average bond enthalpies in  $\text{kJ mol}^{-1}$ 

	H	C	N	O	F	Cl	Br	I	S	P
H	436									
C	415	348(s) 612(d) 838(t) 518(ar)								
N	391	292(s) 614(d) 890(t)	161(s) 413(d) 946(t)							
O	463	355(s) 734(d)	166	145(s) 497(d)						
F	565	484	270	185	156					
Cl	431	333	200	203	254	243				
Br	366	276				219	193			
I	299	238				210	178	151		
S	353	259			496	250	212		265	
P	322									201

(s) single bond, (d) double bond, (t) triple bond, (ar) aromatic bond

Data: Pauling, L. *General Chemistry*, 3d, ed., Freeman, San Francisco, 1970; Atkins, P. *Physical Chemistry*, 5th, ed., Freeman, New York, 1994. Where the data differ, averages are taken.