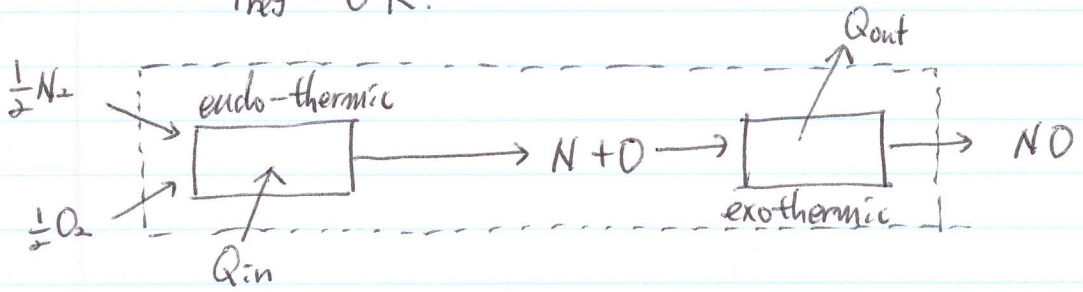
< Thermochemistry II >

* NO formation reaction.

$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow NO.$

$\Rightarrow \frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow N + O \rightarrow NO.$

$T_{ref} = 0\,K.$



0K. 0K

- Q_{in} is used for dissociation reaction

$$Q_{in} = \frac{1}{2}(D_0)_{N_2} + \frac{1}{2}(D_0)_{O_2}$$

Bond energy.

- Q_{out} is extracted from the mixture to lower temperature to 0K.

$= (-D_0)_{NO}$

< First law. >

$$\frac{1}{2} h_{N_2}(0K) + \frac{1}{2} h_{O_2}(0K) + Q_{in} = h_{NO}(0K) + Q_{out}$$

$$Q_{in} - Q_{out} = \frac{1}{2}\left((D_0)_{N_2} + (D_0)_{O_2}\right) - (D_0)_{NO}$$

$$= h_{NO}(0K) - \frac{1}{2}\left(h_{N_2}(0K) + h_{O_2}(0K)\right) = \boxed{\Delta_f H_{NO}(0K)}$$

$\equiv$ Net Q_{in}

* How to calculate $\Delta_f H_{NO}(298K)$?

$$= h_{NO}(298K) - \frac{1}{2}\left(h_{N_2}(298K) + h_{O_2}(298K)\right)$$

$\Delta_f H_{NO}(0K)$ is known! $\because$ D_0 N_2, O_2, NO are known.

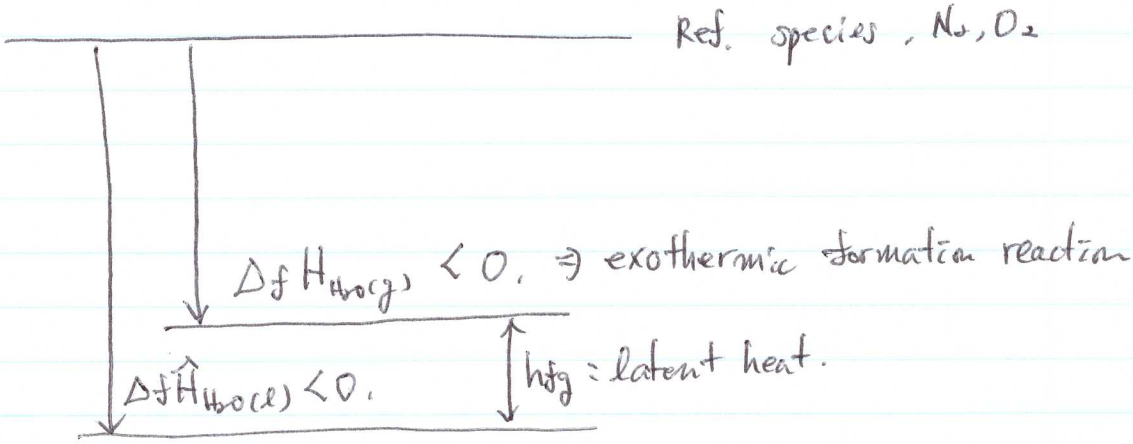
$$\Delta_f H_{NO}(298K) - \Delta_f H_{NO}(0K)$$
$$= \underbrace{h_{NO}(298K) - h_{NO}(0K)}_{\Delta E_{chem} = 0} - \frac{1}{2}\Big(\underbrace{(h_{N_2}(298K) - h_{N_2}(0K))}_{\Delta E_{chem} = 0} + \underbrace{(h_{O_2}(298K) - h_{O_2}(0K))}_{\Delta E_{chem} = 0}\Big)$$

$\therefore$ $\Rightarrow$ difference of sensible enthalpy.

- latent heat.

when with a phase change during Qout process, latent heat should be considered

ex) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (liquid or gas)



what if $\Delta_f H > 0$. $\Rightarrow$ endothermic formation reaction

e.g.) O, N, H, S, atoms. O_3 etc.

- Heat of Reaction.

$$\Delta H_R \equiv H_{prod}(298K) - H_{react}(298K)$$

ex) $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O(g) + 7.52N_2$

Reactant. 298 K — Product. 298 K

$$\Delta H_R = \Delta_f H_{CO_2} + 2\Delta_f H_{H_2O} - \Delta_f H_{CH_4} \quad @298\,K$$

O_2, N_2 are reference species.
$\Rightarrow \Delta_f H_{O_2} = \Delta_f H_{N_2} = 0$. regardless of temperature.

why? no chemical energy difference.

$$\underset{T_r}{O_2} \xrightarrow{\Downarrow} \underset{T_p}{O_2}$$

No sensible enthapy difference.

and $T_r = T_p = T$ for formation reaction

$\therefore \Delta_f H_{O_2}(T) = 0$ @ any T.

$\Delta H_R > 0$: endothermic reaction $\therefore$ Q_{out} is larger than Q_{in} $\Rightarrow Q_{in} > Q_{out}$.

$\Delta H_R < 0$: exothermic reaction $\Rightarrow Q_{in} > Q_{out}$.

- Thermochemical properties.
  - Bond Energy
  - Heat of Reaction

$$C_nH_m + \underline{(n + m/4)}(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O.$$

$$\Delta H_R(298K) = \sum_{i} \nu_i' \Delta_f H_i(298K) - \Delta_f H_{C_nH_m}(298K)$$

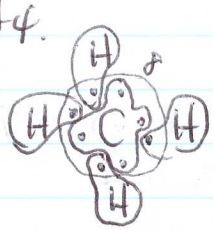
product species

* Lewis Diagram.

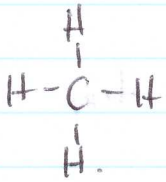
C	H	N	O
4	1	5	6

e on outer shell

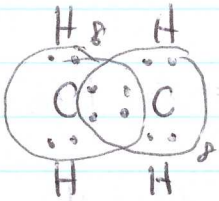
- CH_4.

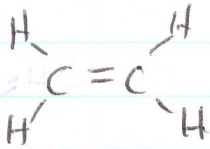


δ e make the bonds complete.



- C_2H_4

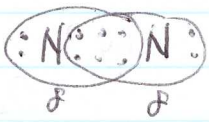




- H_2

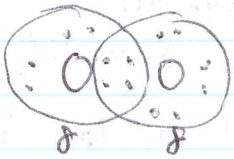
H − H.

- N_2



N ≡ N

- O_2



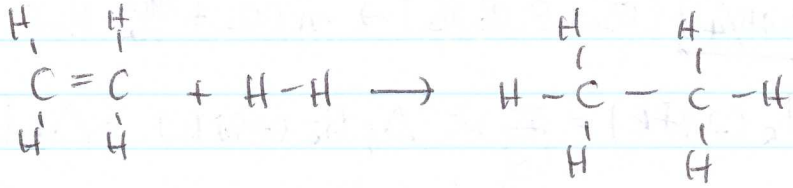
O = O.

Average Bond Energy.

e.g.)

C − H	410 kJ/mol
C = C	594 kJ/mol
C − C	335 kJ/mol
H − H	432 kJ/mol

$C_2H_4 + H_2 \longrightarrow C_2H_6$



$1(C=C) + 4(C-H) + 1(H-H) \longrightarrow 1(C-C) + 6(C-H)$

$594 + 4 \times 410 + 432 \rightarrow 335 + 6 \times 410.$

2666 kJ/mol 2795 kJ/mol

$\Delta H_R \approx \sum_{react.} (\text{Bond } \bar{E}) - \sum_{prod.} (\text{Bond } \bar{E}) = (-129 \text{ kJ/mol})$

$= H_{prod} - H_{react} = -137.2$ kJ using table 1.1.

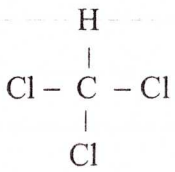
* Cp , ΔfH , S can be estimated using similar approache.

Partial Bond Contributions for the Estimation of $\hat{c}_p$, $\hat{S}^o$, and $\Delta_f\hat{H}$ of Gas-Phase Species at 298K, 1 bar

Bond	$\hat{c}_p$(298K) - J/mol K	$\hat{S}^o$ - J/mol K	$\Delta_f\hat{H}$(298K) - kJ/mol
C-H	7.28	53.97	−16.0
C-C	8.28	−68.62	11.4
C-F	13.97	70.71	−219.7
C-Cl	19.41	82.42	−31.0
C-O	11.30	−16.74	−50.2
O-H	11.30	100.42	−113.0
O-O	20.50	38.07	90.0
O-Cl	23.00	135.98	38.1
C-N	8.79	−53.56	38.9
N-H	9.62	74.06	−10.9
C-S	14.23	−6.28	28.0
S-H	13.39	112.97	−3.3

Data from *Thermochemical Kinetics, 2nd Edition*, S. W. Benson, John Wiley, 1976.

To illustrate the use of this table, let us calculate $\Delta_f\hat{H}$ (298K) and $\hat{c}_p$ (298K) for chloroform (trichloromethane), $CHCl_3$. The bond structure of chloroform is



Hence, the molecule contains 3 C–Cl bonds and 1 C–H bond. It follows from the bond additivity model that,

$$\Delta_f\hat{H}(298K) = (3)\,\Delta_f\hat{H}(C\text{–}Cl) + (1)\,\Delta_f\hat{H}(C\text{–}H)$$
$$= (3)(-31.0\text{ kJ/mol}) + (1)(-16.0\text{ kJ/mol}) = -109.0\text{ kJ/mol}$$
$$\hat{c}_p(298K) = (3)\,\hat{c}_p(C\text{–}Cl) + (1)\,\hat{c}_p(C\text{–}H)$$
$$= (3)(19.41\text{ J/mol K}) + (1)(7.28\text{ J/mol K}) = 65.51\text{ J/mol K}$$

* This approach (bond additivity) does not account for interactions between bonds.
⇒ * group additivity model.

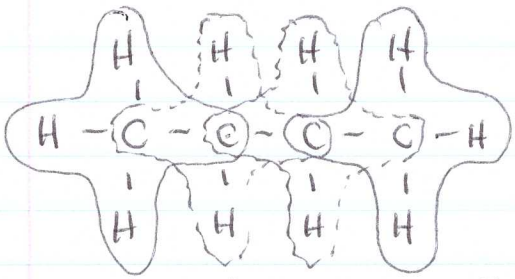
* Group Additivity Model

Representative Group Contributions to $\Delta_f\hat{H}(298K)$ and $\hat{c}_p(300K)$

Group	$\Delta_f\hat{H}(298K)$ - kJ/mol	$\hat{c}_p(300K)$ - J/mol K
$C\text{-}(H)_3(C)$	−42.68	25.90
$C\text{-}(H)_2(C)_2$	−20.63	23.01
$C\text{-}(H)(C)_3$	−7.95	19.00
$C\text{-}(C)_4$	2.09	18.28
$C_d\text{-}(H)_2$	26.19	21.34
$C_d\text{-}(H)(C)$	35.94	17.41
$C_d\text{-}(C)_2$	43.26	17.15
$C_t\text{-}(H)$	112.68	22.05
$C_t\text{-}(C)$	115.27	13.10
$C\text{-}(N)(H)_3$	−42.17	25.90
$C\text{-}(N)(C)(H)_2$	−27.61	21.97
$N\text{-}(N)(H)_2$	47.70	25.52
$C\text{-}(F)_3(C)$	−662.75	53.14
$C\text{-}(Cl)_3(C)$	−86.61	68.20
$C\text{-}(Cl)_2(H)(C)$	−79.08	50.63
$C\text{-}(Cl)(H)_2(C)$	−69.04	37.24
$C\text{-}(Cl)(H)(C)_2$	−61.92	37.66
$C\text{-}(H)_3(O)$	−42.17	25.90
$O\text{-}(H)(C)$	−158.57	17.99

Data from *Thermochemical Kinetics, 2nd Edition*, S. W. Benson, John Wiley, 1976.

ex) C_4H_{10}



$C\text{-}(H)_3(C)$ $C\text{-}H_3(C)$

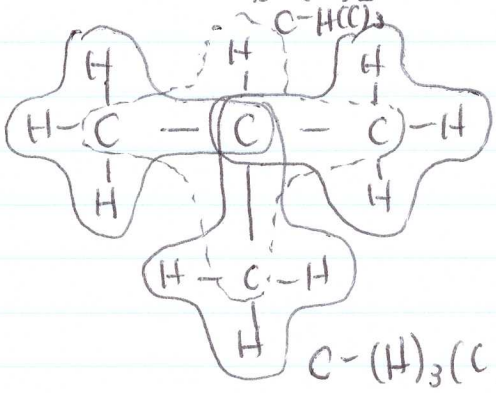
$C\text{-}(H_2)(C)_2$

$\therefore \Delta_f H(298k)$

$= 2\times(-42.68) + 2\times(-20.63)$

$= (-126.62\ KJ/mol)$

$C\text{-}H(C)_3$



$C\text{-}(H)_3(C)$

$\therefore \Delta_f H(298k)$

$= 3\times(-42.68) + (-7.95) = (-136\ KJ/mol)$

- <u>Adiabatic</u> Combustion Temperature

  ↳ $Q_{in/out} = 0$.

  $T_{react} \neq T_{product}$.

  $T_1 \neq T_2$

  $H_{react}(T_1) = H_{prod}(T_2)$

  T_2 = adiabatic combustion temp.

$$H_{prod} = \sum_i \nu_i' h_i(T_2) \quad , \quad H_{reac} = \sum_i \nu_i h_i(T_1)$$

$$h_i(T) = \Delta_f H_i(T_{ref}) + \left(h_i(T) - h_i(T_{ref}) \right)_{sens}.$$

Assume $T_1 = T_{ref} = 298K$.

$$\left[\sum_i \nu_i' \int_{T_1}^{T_2} C_{p_i}\, dT \right]_{prod} = \left[\sum_i \nu_i \Delta_f H_i(\underset{T_{ref}}{T_1}) \right]_{react} - \left[\sum_i \nu_i' \Delta_f H_i(T_r) \right]_{prod}$$

$$= -\Delta H_R(\underset{T_1 = T_{ref}}{298K}) = \text{known!!}$$

- Product gas composition.

In stoichiometric or lean mixture, straightforward

* $\phi = 1$. $C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 18.8N_2$.
* $\phi < 1$.

$$\phi\, C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3\phi\, CO_2 + 4\phi\, H_2O + 18.8N_2 + 5(1-\phi)\, O_2.$$

CO_2 concentration

$$= \frac{3\phi}{3\phi + 4\phi + 18.8 + 5(1-\phi)}$$

what if $\phi > 1$ (rich)

$$\phi\, C_3H_8 + 5(O_2 + 3.76\, N_2)$$
$$\rightarrow a\, CO_2 + b\, CO + c\, H_2O + d\, H_2 + 18.8\, N_2$$

dominant species assumption.

* Atom Conservation

$C: 3\phi = a + b$
$H: 8\phi = 2c + 2d$
$O: 10 = 2a + b + c$

* Chemical Equilibrium.
Water Gas Reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$ ⇐ 4 dominant product species.

$$K_p(T) = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{a \cdot d}{b \cdot c}$$ = equilibrium constant.

TABLE 1.1. Enthalpy of Formation of Various Substances at 25°C

Substance	Formula	State	$\Delta_f \hat{H}°$ (kJ/mol)
Carbon monoxide	CO	g	−110.53
Carbon dioxide	CO_2	g	−393.52
Hydrogen	H_2*	g	0
Methane	CH_4	g	− 74.87
Ethane	C_2H_6	g	− 84.67
Propane	C_3H_8	g	−103.80
n-Butane	C_4H_{10}	g	−124.73
i-Butane	C_4H_{10}	g	−131.59
n-Pentane	C_5H_{12}	g	−146.44
n-Hexane	C_6H_{14}	g	−166.94
n-Heptane	C_7H_{16}	g	−187.86
n-Octane	C_8H_{18}	l	−250.37
n-Octane	C_8H_{18}	g	−208.40
i-Octane	C_8H_{18}	g	−224.14
Acetylene (Ethyne)	C_2H_2	g	226.73
Ethylene (Ethene)	C_2H_4	g	52.47
Benzene	C_6H_6	g	82.93
Methanol	CH_3OH	l	−238.57
Methanol	CH_3OH	g	−200.58
Ethanol	C_2H_6O	l	−277.65
Oxygen	O_2*	g	0
Nitrogen	N_2*	g	0
Carbon (graphite)	C*	crystalline	0
Water	H_2O	g	−241.83
Water	H_2O	l	−285.83
Chlorine	Cl_2*	g	0
Hydrogen chloride	HCl	g	− 92.31
Carbon tetrachloride	CCl_4	g	− 95.98
Dichloromethane	CH_2Cl_2	g	− 95.52
Nitric oxide	NO	g	90.29
Nitrogen dioxide	NO_2	g	33.10
Nitrous oxide	N_2O	g	82.05
Ammonia	NH_3	g	− 45.90
Hydroxyl radical	OH	g	38.99
Sulfur (orthorhombic)	S*	crystalline	0
Sulfur monoxide	SO	g	5.01
Sulfur dioxide	SO_2	g	−296.84
Sulfur trioxide	SO_3	g	−395.76
Ozone	O_3	g	142.67
Carbon (atom)	C	g	716.67
Oxygen (atom)	O	g	249.17
Nitrogen (atom)	N	g	472.68
Hydrogen (atom)	H	g	218.00
Chlorine (atom)	Cl	g	121.30
Sulfur (atom)	S	g	276.98

* JANAF-NIST reference species