

2.13: Some Concepts in Thermochemistry

Chemical reactions and the law of mass action

Suppose we have a chemical reaction among σ species, written as

$$\zeta_1 A_1 + \zeta_2 A_2 + \cdots + \zeta_\sigma A_\sigma = 0, \quad (2.13.1)$$

where

$$\begin{aligned} A_a &= \text{chemical formula} \\ \zeta_a &= \text{stoichiometric coefficient} . \end{aligned}$$

For example, we could have

$$-3 H_2 - N_2 + 2 NH_3 = 0 \quad (3 H_2 + N_2 \rightleftharpoons 2 NH_3) \quad (2.13.2)$$

for which

$$\zeta(H_2) = -3, \quad \zeta(N_2) = -1, \quad \zeta(NH_3) = 2. \quad (2.13.3)$$

When $\zeta_a > 0$, the corresponding A_a is a *product*; when $\zeta_a < 0$, the corresponding A_a is a *reactant*. The bookkeeping of the coefficients ζ_a which ensures conservation of each individual species of atom in the reaction(s) is known as *stoichiometry*²⁵

Now we ask: what are the conditions for equilibrium? At constant T and p , which is typical for many chemical reactions, the conditions are that $G(T, p, \{N_a\})$ be a minimum. Now

$$dG = -S dT + V dp + \sum_i \mu_a dN_a, \quad (2.13.4)$$

so if we let the reaction go forward, we have $dN_a = \zeta_a$, and if it runs in reverse we have $dN_a = -\zeta_a$. Thus, setting $dT = dp = 0$, we have the equilibrium condition

$$\sum_{a=1}^{\sigma} \zeta_a \mu_a = 0. \quad (2.13.5)$$

Let us investigate the consequences of this relation for ideal gases. The chemical potential of the $\boxed{a^{\text{ssr}}\{\text{th}\}}$ species is

$$\mu_a(T, p) = k_B T \phi_a(T) + k_B T \ln p_a. \quad (2.13.6)$$

Here $p_a = p x_a$ is the partial pressure of species a , where $x_a = N_a / \sum_b N_b$ the dimensionless concentration of species a . Chemists sometimes write $x_a = [A_a]$ for the concentration of species a . In equilibrium we must have

$$\sum_a \zeta_a [\ln p + \ln x_a + \phi_a(T)] = 0, \quad (2.13.7)$$

which says

$$\sum_a \zeta_a \ln x_a = - \sum_a \zeta_a \ln p - \sum_a \zeta_a \phi_a(T). \quad (2.13.8)$$

Exponentiating, we obtain the *law of mass action*:

$$\prod_a x_a^{\zeta_a} = p^{-\sum_a \zeta_a} \exp\left(-\sum_a \zeta_a \phi_a(T)\right) \equiv \kappa(p, T). \quad (2.13.9)$$

The quantity $\kappa(p, T)$ is called the *equilibrium constant*. When κ is large, the LHS of the above equation is large. This favors maximal concentration x_a for the products ($\zeta_a > 0$) and minimal concentration x_a for the reactants ($\zeta_a < 0$). This means that the equation REACTANTS \rightleftharpoons PRODUCTS is shifted to the right, the products are plentiful and the reactants are scarce. When κ is small, the LHS is small and the reaction is shifted to the left, the reactants are plentiful and the products are scarce. Remember we are describing *equilibrium conditions* here. Now we observe that reactions for which $\sum_a \zeta_a > 0$ shift to the left with increasing pressure and shift to the right with decreasing pressure, while reactions for which $\sum_a \zeta_a < 0$ the situation is reversed: they shift to

the right with increasing pressure and to the left with decreasing pressure. When $\sum_a \zeta_a = 0$ there is no shift upon increasing or decreasing pressure.

The rate at which the equilibrium constant changes with temperature is given by

$$\left(\frac{\partial \ln \kappa}{\partial T} \right)_p = - \sum_a \zeta_a \phi'_a(T). \quad (2.13.10)$$

Now from Equation [mui] we have that the enthalpy per particle for species i is

$$h_a = \mu_a - T \left(\frac{\partial \mu_a}{\partial T} \right)_p, \quad (2.13.11)$$

since $\mathcal{H} = G + TS$ and $S = - \left(\frac{\partial G}{\partial T} \right)_p$. We find

$$h_a = -k_B T^2 \phi'_a(T), \quad (2.13.12)$$

and thus

$$\left(\frac{\partial \ln \kappa}{\partial T} \right)_p = \frac{\sum_i \zeta_i h_i}{k_B T^2} = \frac{\Delta h}{k_B T^2}, \quad (2.13.13)$$

where Δh is the enthalpy of the reaction, which is the heat absorbed or emitted as a result of the reaction.

When $\Delta h > 0$ the reaction is *endothermic* and the yield increases with increasing T . When $\Delta h < 0$ the reaction is *exothermic* and the yield decreases with increasing T .

As an example, consider the reaction $H_2 + I_2 \rightleftharpoons 2 HI$. We have

$$\zeta(H_2) = -1, \quad \zeta(I_2) = -1, \quad \zeta(HI) = 2. \quad (2.13.14)$$

Suppose our initial system consists of ν_1^0 moles of H_2 , $\nu_2^0 = 0$ moles of I_2 , and ν_3^0 moles of undissociated HI . These mole numbers determine the initial concentrations x_a^0 , where $x_a = \nu_a / \sum_b \nu_b$. Define

$$\alpha \equiv \frac{x_3^0 - x_3}{x_3}, \quad (2.13.15)$$

in which case we have

$$x_1 = x_1^0 + \frac{1}{2} \alpha x_3^0, \quad x_2 = \frac{1}{2} \alpha x_3^0, \quad x_3 = (1 - \alpha) x_3^0. \quad (2.13.16)$$

Then the law of mass action gives

$$\frac{4(1 - \alpha)^2}{\alpha(\alpha + 2r)} = \kappa. \quad (2.13.17)$$

where $r \equiv x_1^0 / x_3^0 = \nu_1^0 / \nu_3^0$. This yields a quadratic equation, which can be solved to find $\alpha(\kappa, r)$. Note that $\kappa = \kappa(T)$ for this reaction since $\sum_a \zeta_a = 0$. The enthalpy of this reaction is positive: $\Delta h > 0$.

Enthalpy of formation

Most chemical reactions take place under constant pressure. The heat Q_{if} associated with a given isobaric process is

$$Q_{if} = \int_i^f dE + \int_i^f p dV = (E_f - E_i) + p(V_f - V_i) = \mathcal{H}_f - \mathcal{H}_i, \quad (2.13.18)$$

where \mathcal{H} is the *enthalpy*,

$$\mathcal{H} = E + pV. \quad (2.13.19)$$

Note that the enthalpy \mathcal{H} is a state function, since E is a state function and p and V are state variables. Hence, we can meaningfully speak of changes in enthalpy: $\Delta\mathcal{H} = \mathcal{H}_f - \mathcal{H}_i$. If $\Delta\mathcal{H} < 0$ for a given reaction, we call it *exothermic* – this is the case when $Q_{if} < 0$ and thus heat is transferred to the surroundings. Such reactions can occur spontaneously, and, in really fun cases, can produce explosions. The combustion of fuels is always exothermic. If $\Delta\mathcal{H} > 0$, the reaction is called *endothermic*. Endothermic reactions require that heat be supplied in order for the reaction to proceed. Photosynthesis is an example of an endothermic reaction.

[dhtab] Enthalpies of formation of some common substances.

$\Delta\mathcal{H}_f^0$				$\Delta\mathcal{H}_f^0$			
Formula	Name	State	kJ/mol	Formula	Name	State	kJ/mol
Ag	Silver	crystal	0.0	NiSO ₄	Nickel sulfate	crystal	-872.9
C	Graphite	crystal	0.0	Al ₂ O ₃	Aluminum oxide	crystal	-1657.7
C	Diamond	crystal	1.9	Ca ₃ P ₂ O ₈	Calcium phosphate	gas	-4120.8
O ₃	Ozone	gas	142.7	HCN	Hydrogen cyanide	liquid	108.9
H ₂ O	Water	liquid	-285.8	SF ₆	Sulfur hexafluoride	gas	-1220.5
H ₃ BO ₃	Boric acid	crystal	-1094.3	CaF ₂	Calcium fluoride	crystal	-1228.0
ZnSO ₄	Zinc sulfate	crystal	-982.8	CaCl ₂	Calcium chloride	crystal	-795.4

Suppose we have two reactions



and



Then we may write



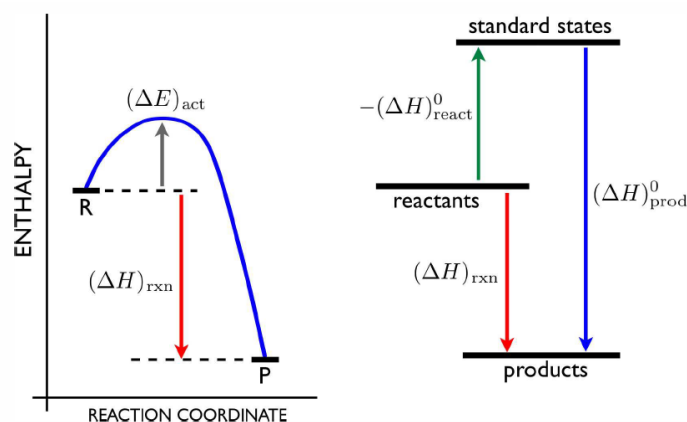
with

$$(\Delta\mathcal{H})_1 + (\Delta\mathcal{H})_2 = (\Delta\mathcal{H})_3 \quad (2.13.23)$$

We can use this additivity of reaction enthalpies to define a *standard molar enthalpy of formation*. We first define the *standard state* of a pure substance at a given temperature to be its state (gas, liquid, or solid) at a pressure $p = 1$ bar. The *standard reaction enthalpies* at a given temperature are then defined to be the reaction enthalpies when the reactants and products are all in their standard states. Finally, we define the *standard molar enthalpy of formation* $\Delta\mathcal{H}_f^0(X)$ of a compound X at temperature T as the reaction enthalpy for the compound X to be produced by its constituents when they are in their standard state. For example, if $X = \text{SO}_2$, then we write

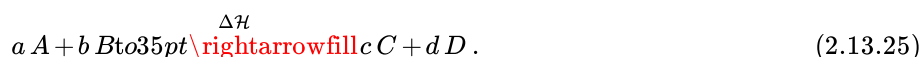


The enthalpy of formation of any substance in its standard state is zero at all temperatures, by definition: $\Delta\mathcal{H}_f^0[\text{O}_2] = \Delta\mathcal{H}_f^0[\text{He}] = \Delta\mathcal{H}_f^0[\text{K}] = \Delta\mathcal{H}_f^0[\text{Mn}] = 0$,



[rxnenthalpy] Left panel: reaction enthalpy and activation energy (exothermic case shown). Right panel: reaction enthalpy as a difference between enthalpy of formation of reactants and products.

Suppose now we have a reaction



To compute the reaction enthalpy $\Delta \mathcal{H}$, we can imagine forming the components A and B from their standard state constituents. Similarly, we can imagine doing the same for C and D . Since the number of atoms of a given kind is conserved in the process, the constituents of the reactants must be the same as those of the products, we have

$$\Delta \mathcal{H} = -a \Delta \mathcal{H}_f^0(A) - b \Delta \mathcal{H}_f^0(B) + c \Delta \mathcal{H}_f^0(C) + d \Delta \mathcal{H}_f^0(D) . \quad (2.13.26)$$

A list of a few enthalpies of formation is provided in table [dhtab]. Note that the reaction enthalpy is independent of the actual reaction path. That is, the difference in enthalpy between A and B is the same whether the reaction is $A \rightarrow B$ or $A \rightarrow X \rightarrow (Y + Z) \rightarrow B$. This statement is known as *Hess's Law*.

Note that

$$d\mathcal{H} = dE + p dV + V dp = \frac{dQ}{dt} + V dp , \quad (2.13.27)$$

hence

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{\partial \mathcal{H}}{\partial T} \right)_p . \quad (2.13.28)$$

We therefore have

$$\mathcal{H}(T, p, \nu) = \mathcal{H}(T_0, p, \nu) + \nu \int_{T_0}^T dT' c_p(T') . \quad (2.13.29)$$

For ideal gases, we have $c_p(T) = (1 + \frac{1}{2}f) R$. For real gases, over a range of temperatures, there are small variations:

$$c_p(T) = \alpha + \beta T + \gamma T^2 . \quad (2.13.30)$$

Two examples ($300 K < T < 1500 K$, $p = 1 \text{ atm}$):

$$\begin{aligned} O_2 : \quad \alpha &= 25.503 \frac{J}{mol K} , \quad \beta = 13.612 \times 10^{-3} \frac{J}{mol K^2} , \quad \gamma = -42.553 \times 10^{-7} \frac{J}{mol K^3} \\ H_2O : \quad \alpha &= 30.206 \frac{J}{mol K} , \quad \beta = 9.936 \times 10^{-3} \frac{J}{mol K^2} , \quad \gamma = 11.14 \times 10^{-7} \frac{J}{mol K^3} \end{aligned}$$

If all the gaseous components in a reaction can be approximated as ideal, then we may write

$$(\Delta \mathcal{H})_{rxn} = (\Delta E)_{rxn} + \sum_a \zeta_a RT , \quad (2.13.31)$$

where the subscript 'rxn' stands for 'reaction'. Here $(\Delta E)_{rxn}$ is the change in energy from reactants to products.

[enthtab] Average bond enthalpies for some common bonds. (Source: L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, NY, 1960).)

	enthalpy		enthalpy		enthalpy		enthalpy
bond	(kJ/mol)	bond	(kJ/mol)	bond	(kJ/mol)	bond	(kJ/mol)
$H-H$	436	$C-C$	348	$C-S$	259	$F-F$	155
$H-C$	412	$C=C$	612	$N-N$	163	$F-Cl$	254
$H-N$	388	$C \equiv C$	811	$N=N$	409	$Cl-Br$	219
$H-O$	463	$C-N$	305	$N \equiv N$	945	$Cl-I$	210
$H-F$	565	$C=N$	613	$N-O$	157	$Cl-S$	250
$H-Cl$	431	$C \equiv N$	890	$N-F$	270	$Br-Br$	193
$H-Br$	366	$C-O$	360	$N-Cl$	200	$Br-I$	178
$H-I$	299	$C=O$	743	$N-Si$	374	$Br-S$	212
$H-S$	338	$C-F$	484	$O-O$	146	$I-I$	151
$H-P$	322	$C-Cl$	338	$O=O$	497	$S-S$	264
$H-Si$	318	$C-Br$	276	$O-F$	185	$P-P$	172
		$C-I$	238	$O-Cl$	203	$Si-Si$	176

Bond enthalpies

The enthalpy needed to break a chemical bond is called the *bond enthalpy*, $h[\bullet]$. The bond enthalpy is the energy required to dissociate one mole of gaseous bonds to form gaseous atoms. A table of bond enthalpies is given in Tab. [enthtab]. Bond enthalpies are endothermic, since energy is required to break chemical bonds. Of course, the actual bond energies can depend on the location of a bond in a given molecule, and the values listed in the table reflect averages over the possible bond environment.

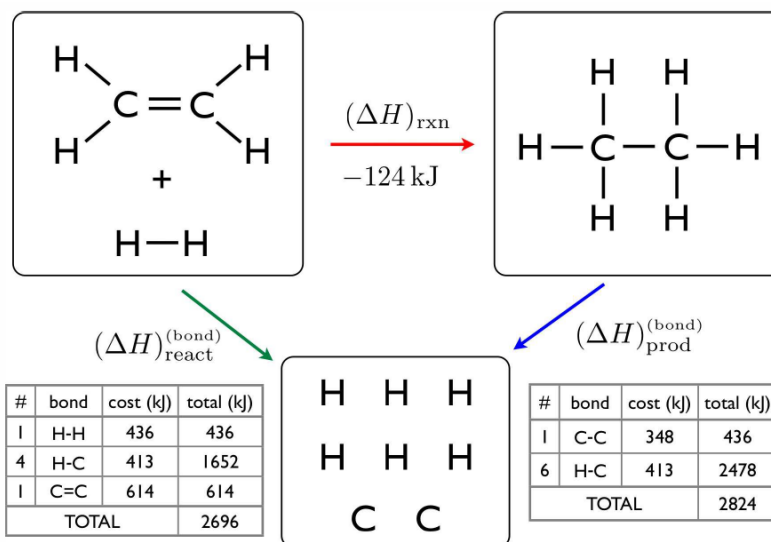
The bond enthalpies in Tab. [enthtab] may be used to compute reaction enthalpies. Consider, for example, the reaction $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$. We then have, from the table,

$$\begin{aligned} (\Delta H)_{rxn} &= 2 h[H-H] + h[O=O] - 4 h[H-O] \\ &= -483 \text{ kJ/mol } O_2. \end{aligned}$$

Thus, 483 kJ of heat would be released for every two moles of H_2O produced, if the H_2O were in the gaseous phase. Since H_2O is liquid at STP, we should also include the condensation energy of the gaseous water vapor into liquid water. At $T = 100^\circ C$ the latent heat of vaporization is $\tilde{\ell} = 2270 \text{ J/g}$, but at $T = 20^\circ C$, one has $\tilde{\ell} = 2450 \text{ J/g}$, hence with $M = 18$ we have $\ell = 44.1 \text{ kJ/mol}$. Therefore, the heat produced by the reaction



$(\Delta H)_{rxn} = -571.2 \text{ kJ/mol } O_2$. Since the reaction produces two moles of water, we conclude that the enthalpy of formation of liquid water at STP is half this value: $\Delta H_f^0[H_2O] = 285.6 \text{ kJ/mol}$.

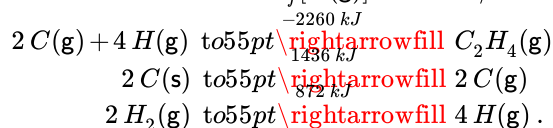


[ethene] Calculation of reaction enthalpy for the hydrogenation of ethene (ethylene), C_2H_4 .

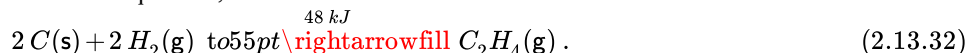
Consider next the hydrogenation of ethene (ethylene): C_2H_4 . The



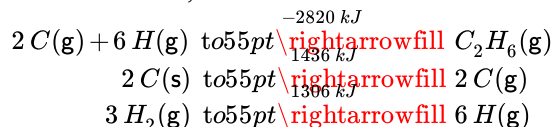
product is known as ethane. The energy accounting is shown in Fig. [ethene]. To compute the enthalpies of formation of ethene and ethane from the bond enthalpies, we need one more bit of information, which is the standard enthalpy of formation of $C(g)$ from $C(s)$, since the solid is the standard state at STP. This value is $\Delta H_f^0[C(g)] = 718 \text{ kJ/mol}$. We may now write



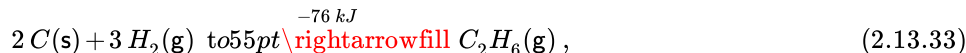
Thus, using Hess's law, adding up these reaction equations, we have



Thus, the formation of ethene is endothermic. For ethane,



For ethane,



which is exothermic.

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