

Chemistry 223: Thermochemistry

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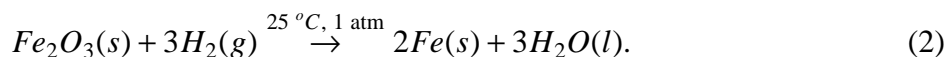
1. Enthalpy Calculations: Chemical Reactions and Hess' Law

The enthalpy change for a process, ΔH , is equal to the heat absorbed by the system if that process is done under constant pressure conditions (and assuming that only P-V work is possible). Since the enthalpy of a system, $H = E + PV$, is a state function, we can systematize enthalpy calculations by considering a path whereby the compounds first turn into their constituent elements in their standard states (by convention at 25 °C and 1 atm pressure) and then recombine to form the products. The enthalpy change in the latter step is just the enthalpy of formation of the products and the former is the enthalpy of destruction (i.e., the negative of the enthalpy of formation) of the reactants. Hence,

$$\Delta H = \sum \left[\Delta H_f^0(\text{products}) - \Delta H_f^0(\text{reactants}) \right]. \quad (1)$$

Since we are interested in calculating a difference, the absolute enthalpy of the elements in their standard states is unimportant [it cancels out of Eq. (1)], and we adopt the convention that the enthalpy of formation of an element in its standard state is zero.

Consider the following example (reduction of iron oxide):



A table of thermochemical data gives:

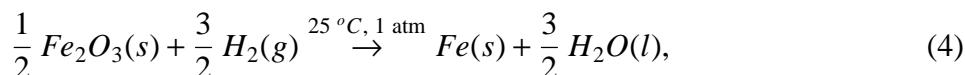
Enthalpies of Formation at 1 atm and 25 C

Compound	ΔH_f^0 (kJ/mol)
$Fe_2O_3(s)$	-824.2
$H_2(g)$	0.0
$Fe(s)$	0.0
$H_2O(l)$	-285.830

By using these in Eq. (1), we find that

$$\Delta H = [3(-285.830) - (-824.2)] \text{kJ/mol} = -33.29 \text{kJ/mol}. \quad (3)$$

Note that the calculated enthalpy change depends on how the reaction was written. For example, if we wrote

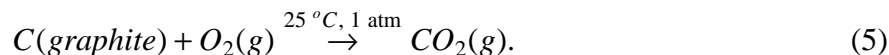


then $\Delta H = -16.65 \text{ kJ/mol}$.

2. Measuring ΔH_f^0

There are a number of ways in which to measure the enthalpy of formation of a compound; here are two. The most obvious is to simply carry out the formation reaction from the constituent elements in their standard states in a constant pressure calorimeter (recall that $\Delta H = Q_p$).

For example, consider the combustion of graphite to form carbon dioxide



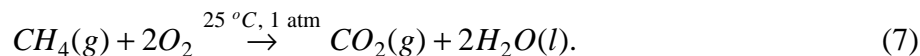
The heat released in this reaction is $-\Delta H_f^0(CO_2)$, since the standard enthalpy of formation of the reactants is zero. Note that the enthalpy change in this sort of reaction is also referred to as the heat of combustion.

For this method to work, two conditions must be met: 1) the reaction goes to completion and 2) only one product is formed. Thus, the reaction



is not suitable for this method since it doesn't readily go to completion and we get a complicated mixture of hydrocarbons.

In order to get around this, note that it is often possible to burn something to completion (and measure $\Delta H_{\text{combustion}}$, the heat released). Thus consider



Equation (1) gives

$$\Delta H_{\text{combustion}} = \Delta H_f^0(CO_2(g)) + 2\Delta H_f^0(H_2O(l)) - \Delta H_f^0(CH_4(g)). \quad (8)$$

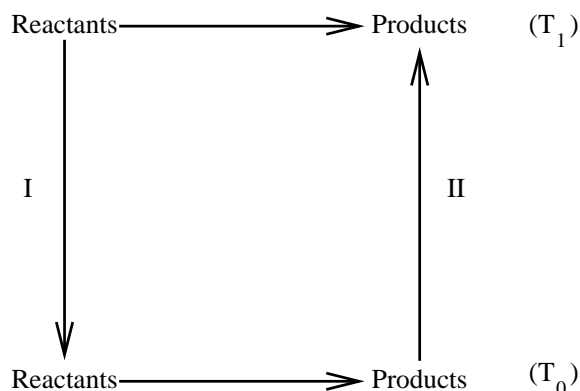
The standard enthalpies of formation of carbon dioxide and water can be measured using the first method; hence, once we measure the heat of combustion, the only unknown is the standard enthalpy of formation of methane (CH_4) and a little algebra gives:

$$\begin{aligned} \Delta H_f^0(CH_4(g)) &= \Delta H_f^0(CO_2(g)) + 2\Delta H_f^0(H_2O(l)) - \Delta H_{\text{combustion}} \\ &= [-398.51 + 2(-285.83) - (-890.36)]\text{kJ/mol} = -74.81\text{kJ/mol} \end{aligned} \quad (9)$$

In general, in order to measure the enthalpy of formation, all you need to do is find any reaction where all but one of the standard enthalpies of formation are known and where the reaction goes to completion. These sorts of manipulations are valid because the enthalpy is a state function, and are referred to as Hess's law. Also note that the same arguments could be made for the energy changes (under constant volume conditions).

3. Reactions at Different Temperatures: Kirchoff's Law

What happens if the temperature at which you perform the reaction (either at constant P or V) is different than that of your table of enthalpies of formation. Since the enthalpy is a state function, an alternate path can be found whereby the enthalpy change, calculated using the temperature of your table, can be used. Consider the constant pressure case depicted below



The enthalpy change for the reaction at T_1 is equal to the enthalpy change at T_0 plus the enthalpy change for paths 1 and 2. However, on 1 or 2, only the constant pressure heating or cooling of the reactants or products is performed (i.e., no chemical reaction takes place). Since the constant pressure heat capacity, C_P was defined as

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_{P,N}, \quad (10)$$

the incremental heat absorbed by the system on 1 or 2 is $C_P dT$. Integrating gives:

$$\Delta H_1 = \int_{T_1}^{T_0} C_P(\text{reactants}) dT = - \int_{T_0}^{T_1} C_P(\text{reactants}) dT \quad (11)$$

and

$$\Delta H_2 = \int_{T_0}^{T_1} C_P(\text{products}) dT. \quad (12)$$

Adding the contributions together gives

$$\Delta H(T_1) = \Delta H(T_0) + \int_{T_0}^{T_1} [C_P(\text{products}) - C_P(\text{reactants})] dT. \quad (13)$$

This is known as Kirchoff's law. What changes must be made for the energy?

Consider our example of the reduction of Fe_2O_3 . What is the enthalpy change at 358K? We will assume that the heat capacities are constant over the temperature range 298 - 358 K.

Constant Pressure Heat Capacities at 1 atm and 25 C

Compound	C_P (J/mol/K)
$Fe_2O_3(s)$	103.8
$H_2(g)$	28.8
$Fe(s)$	25.1
$H_2O(l)$	75.3

Note that elements in their standard states do *not* have zero heat capacities. Using the data in the table, and the result of our earlier calculation gives

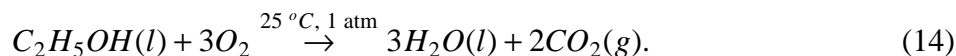
$$\Delta H_{rxn}(358K) = -33.29 + \frac{[2(25.1) + 3(75.3) - 103.8 - 3(28.8)][358 - 298]}{1000}$$

$$= -28.1 \text{ kJ/mol.}$$

Note that no change in phase occurred when we cooled (heated) the reactants (products). What changes would have to be made if the reaction was carried out at 400 K?

4. Bond Energies

Consider the combustion reaction of ethanol:



The standard enthalpies of formation for these compounds are:

Standard Enthalpies of Formation at 25C	
Compound	ΔH_f^0 (kJ/mol)
$C_2H_5OH(l)$	-277.7
$H_2O(l)$	-285.830
$CO_2(g)$	-393.51

which gives $\Delta H_{combustion} = 3 \times (-285.830) + 2 \times (-393.51) - (-277.7) = -1389 \text{ kJ/mol}$ for the reaction as written. This is quite exothermic. Where does the energy come from? If you've been told that it's related to breaking bonds, you've been misinformed; as our example clearly shows, it comes from forming bonds, specifically the strong bonds in CO_2 and H_2O .

We can make this idea more quantitative as by considering the typical energies in bonds. This is a useful, albeit very approximate, way to calculate enthalpy changes in chemical reactions. Consider the following reaction



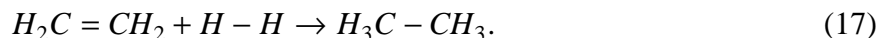
i.e., one C-H bond is broken. Experimentally, ΔH for this reaction is 102 kcal/mol. Similarly, $\Delta H = 96$ kcal/mol for



A survey of such reactions will show that the heat required to break a single C-H bond is in the range 96-102 kcal/mol. We can thus assign 98 kcal/mol as an average bond energy for the C-H bond. Similar trends are observed in the bond strength of other types of bonds, and the results are summarized in the following table

Average Bond Energies			
Bond	Energy (kcal/mol)	Bond	Energy (kcal/mol)
H-H	103	C-H	98
C-C	80	N-H	92
C=C	145	O-H	109
$C \equiv C$	198	Cl-H	102
N-N	37	Br-H	87
$N \equiv N$	225	I-H	71
O-O	34	C-Cl	78
O=O	117	C-N	66
Cl-Cl	57	$C \equiv N$	210
Br-Br	45	C-O	79
I-I	35	C=O	173

How can this be used? Consider the hydrogenation of ethylene:



At the molecular level, we break one H-H and one C=C bond, and form one C-C and two C-H bonds. The energy change is just the net energy left in the molecule in such a process. From the table, the bond breaking steps take $145+103=248$ kcal/mol. The bond formation will give off $80+2(98)=276$ kcal/mol. Hence the net energy change in the system is $248-276 = -28$ kcal/mol. To get the enthalpy change, note that at constant pressure,

$$\Delta H = \Delta E + P\Delta V. \quad (18)$$

For this reaction, all reactants and products are gases. If we assume that the gases are ideal, we can compute ΔV ; i.e.,

$$\Delta V = \frac{RT}{P} \Delta N. \quad (19)$$

Here $\Delta N = -1$ and thus

$$\Delta H = -28 - 1.9872 \times 10^{-3} \text{ kcal/mol/K} \times 298K = -28.6 \text{ kcal/mol.}$$

(Note that here the difference between ΔH and ΔE is relatively small). The correct answer is -32.7 kcal/mol. Thus, while the bond energy method is not exact, it gives a reasonable estimate. The reason for the discrepancy is the assumption that the bond energy doesn't depend on what other bonds are present in the molecule--in general this is not true.

5. Some Manipulations Involving Thermodynamic Functions

5.1. The relationship between C_P and C_V

We know that

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \quad \text{and that} \quad C_P = \left(\frac{\partial H}{\partial T} \right)_{N,P}. \quad (20)$$

How these two quantities are related is a good exercise in manipulating thermodynamic

functions. Since $H \equiv E + PV$,

$$C_P = \left(\frac{\partial E}{\partial T} \right)_{N,P} + P \left(\frac{\partial V}{\partial T} \right)_{N,P}, \quad (21)$$

where the last derivative should be recognized as $V\alpha$, where α is the thermal expansion coefficient,

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{N,P}. \quad (22)$$

If we view the energy as a function of N, V, T ,

$$\left(\frac{\partial E}{\partial T} \right)_{N,P} = \left(\frac{\partial E}{\partial T} \right)_{N,V} + \left(\frac{\partial E}{\partial V} \right)_{N,T} \left(\frac{\partial V}{\partial T} \right)_{N,P} = C_V + \alpha V \left(\frac{\partial E}{\partial V} \right)_{N,T}. \quad (23)$$

Hence,

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V} \right)_{N,T} \right] \alpha V = \frac{VT\alpha^2}{\kappa}, \quad (24)$$

where

$$\kappa \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} \quad (25)$$

is the isothermal compressibility, and where the last equality will be proven later. The compressibility must be positive (i.e., things get smaller when squeezed) and this implies that $C_P \geq C_V$. For an ideal gas, Joule showed that the internal energy per mol did not depend on the volume. In this case,

$$\bar{C}_P - \bar{C}_V = \alpha P \bar{V} = R. \quad (26)$$

5.2. The Joule-Thompson Experiment

Consider the following adiabatic (i.e, $Q=0$) process, whereby a gas is squeezed through a porous, rigid plug. Initially all the gas is in the left chamber, and is pushed by the piston through the porous plug, exerting a constant pressure, P_1 . As this happens, the piston in the right chamber is withdrawn under constant pressure, P_2 . Note that P_1 and P_2 are the opposing pressures discussed earlier, although the initial and final system pressures will be P_1 and P_2 , respectively.

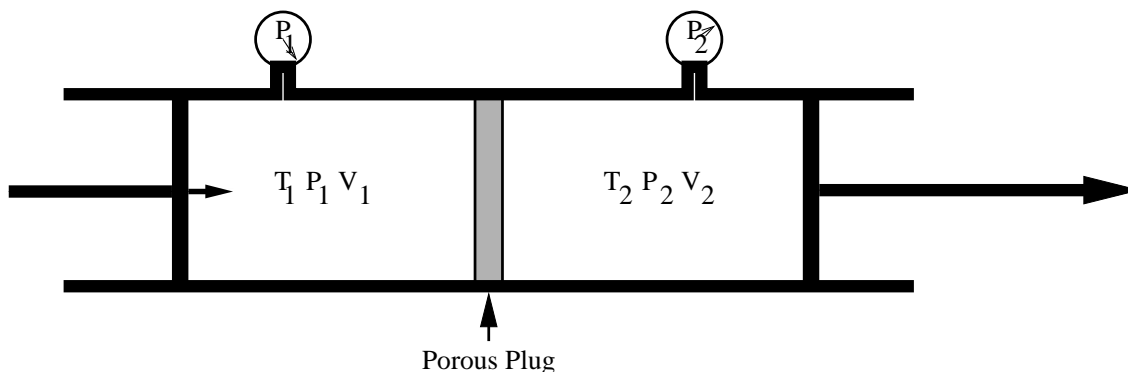


Fig. 1. The Joule-Thomson Experiment. Initially, the piston on the right is against the porous plug and the one on the left is withdrawn. As the experiment progresses, the piston on the left is moved in, keeping the pressure in the left chamber at P_1 , and the one on the right is withdrawn, keeping the pressure in the right chamber at P_2 .

Since, by assumption, $Q=0$,

$$\Delta E = E(P_2, V_2) - E(P_1, V_1) = W = P_1 V_1 - P_2 V_2. \quad (27)$$

By rearranging this expression we can show that

$$E(P_1, V_1) + P_1 V_1 = E(P_2, V_2) + P_2 V_2; \quad (28)$$

i.e., the enthalpy, H , is constant in the Joule-Thomson expansion.

In practice, large temperature changes can be obtained in this type of expansion (which can be used in designing a refrigerator or in liquefying gases). The key parameter is the so-called Joule-Thomson coefficient:

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_{H,N}. \quad (29)$$

In order to express μ_{JT} in terms of more readily measurable quantities, note that

$$\left(\frac{\partial y}{\partial x} \right)_f = - \frac{\left(\frac{\partial f}{\partial x} \right)_y}{\left(\frac{\partial f}{\partial y} \right)_x}, \quad (30)$$

which is sometimes known as the "cyclic rule" or "implicit function differentiation." It is proved by noting that

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy, \quad (31)$$

setting $df=0$, and by solving for the ratio dy/dx .

By using the cyclic rule in Eq. (29), we find that

$$\begin{aligned}\mu_{JT} &= -\frac{\left(\frac{\partial H}{\partial P}\right)_{T,N}}{\left(\frac{\partial H}{\partial T}\right)_{P,N}} = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_{N,T} = -\frac{V}{C_P} \left\{ 1 - \kappa \left[P + \left(\frac{\partial E}{\partial V}\right)_{N,T} \right] \right\} \\ &= -\frac{V}{C_P} \left[1 - \frac{\kappa}{\alpha V} (C_P - C_V) \right] = -\frac{V}{C_P} [1 - \alpha T],\end{aligned}\quad (32)$$

where the second to last equality follows when the definition of the enthalpy in terms of the energy is used and the manipulations used in calculating $C_P - C_V$ are repeated. κ is the isothermal compressibility. Note that the Joule-Thompson coefficient vanishes for an ideal-gas. This is not surprising given the kinetic theory of gases point of view; namely, we know that $\bar{E} = \frac{3}{2} RT$ and $\bar{H} = \bar{E} + PV/N = \frac{5}{2} RT$; hence, keeping H (and N) constant implies that T is constant.

It is interesting to consider physically why the non-ideal gas can change its temperature. According to problem 7.30 in Castellan, $\mu_{JT} = (2a/RT - b)/\bar{C}_p$ for the van der Waals gas. Thus, at low enough temperatures, it is the attractions and the van der Waals dimers that dominate μ_{JT} through the "a" coefficient. When we expand the gas, these dimers will dissociate and this requires energy; since the process is adiabatic, the only place where this energy can be obtained is from the kinetic energy of the gas, and hence, the temperature drops with a drop in pressure (i.e., $\mu_{JT} > 0$). At higher temperatures the steric interactions dominate; these are high-energy configurations, and reducing the pressure leads to these breaking up, releasing their energy to the system, thereby raising the temperature ($\mu_{JT} < 0$).

Note that the expression we just used for μ_{JT} is only valid for very dilute gases (with the usual caveats about the accuracy of the van der Waals equation). In general, there are higher order density corrections, and a more complete expression can be found by applying the cyclic rule to α , i.e.,

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N} = -\frac{1}{V} \left(\frac{\partial P}{\partial T}\right)_{V,N} \div \left(\frac{\partial P}{\partial V}\right)_{T,N}.\quad (33)$$

By applying this to the van der Waals equation of state,

$$P = \frac{NRT}{V - Nb} - a\left(\frac{N}{V}\right)^2,\quad (34)$$

using the result in our last expression for μ_{JT} , and carrying out some simple algebra, we find that

$$\mu_{JT} = \frac{T_i(1 - b\rho)^2 - T}{\bar{C}_p[T - T_i b\rho(1 - b\rho)^2]},\quad (35)$$

where $\rho \equiv N/V$ is the molar density and $T_i \equiv 2a/(Rb)$ is the inversion temperature (the temperature where the zero density Joule Thompson coefficient changes sign). Thus, we see that finite density systems have lower effective inversion temperatures; indeed by letting $T_i^{eff} \equiv 2a(1 - \rho b)^2/Rb < T_i$, it follows that

$$\mu_{JT} = \frac{1 - T/T_i^{eff}}{\bar{C}_p[T/T_i^{eff} - b\rho]}.\quad (36)$$

