The state functions are basically normal functions which depend on the variables P,T, and V. A simple example is the ideal gas law. ONLY two of the variables can be used simultaneously. Like P is defined by T and V.

$$P = \frac{nRT}{V}$$

we can take derivatives of P with respect of T or V while keeping the other constant

$$\left(\frac{\partial P}{\partial T}\right)_V , \ \left(\frac{\partial P}{\partial V}\right)_T$$

An important quantity is the change of P with respect of dT and dV.

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

We can define isothermal compressibility κ and isobaric volumetric thermal expansion coefficients β as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

For ideal gas $\beta = \frac{1}{T}$ and $\kappa = \frac{1}{P}$.

These can be measured experimentally and some values for solid and liquids are listed in Tables 3.1 and 3.2.

With the equation in the book the derivatives in dP can be written as

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} , \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\kappa V}$$

and

$$dP = \frac{\beta}{\kappa}\,dT - \frac{1}{\kappa V}dV \ \ or \ \ \Delta P = \int_{T_i}^{T_f} \frac{\beta}{\kappa}dT - \int_{V_i}^{V_f} \frac{1}{\kappa V}dV \approx \frac{\beta}{\kappa}\Delta T - \frac{1}{\kappa}\ln\frac{V_f}{V_i}$$

Go through example 3.1.

The change of U with respect of V and T is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

The first derivative is the (constant volume) heat capacity

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

the second derivative is bit more complicated. It can be written as

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

and for ideal gas this term is = 0 (use P=nRT/V). Clearly for gases the dT term is larger.

integral of dU

$$\Delta U = \int_{T_1}^{T_2} C_V(T)\ dT + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$$

Note that for ideal gas U depend only on T

For van der Waals gas, $P = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}$, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nRT}{V-nb}$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{n^2 a}{V^2}$$

and

$$\Delta U_T = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = n^2 a \int_{V_1}^{V_2} \frac{dV}{V^2} = n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

For the size of the two terms for internal energy of N_2 go through example 3.5.

The van der Waals parameters for N_2 are: b=3.87*10^{-5} m^3/mol and a= 0.137 m^6/mol^2. Initial T = 200 K and P= 5.0 bar and final T = 400 K and P= 20.0 bar. n = 1 mol. Now initial V_i = 3.28*10^{-3} m^3 and final V_f = 7.88*10^{-4} m^3 (from the vdW equation, note this is a bit difficult calculation, one need to solve 3'rd order polynome)

$$C_v = \left(22.50 - 1.187 * 10^{-2}\frac{T}{K}\right)\frac{J}{K\ mol}$$

The vdW part $\Delta U_T = n^2 a \left(\frac{1}{V_i} - \frac{1}{V_f}\right) = -132\,J = -0.13\ kJ$

the Cv part : $\int_{T_1}^{T_2} C_V(T)\, dT = \int_{200}^{400} \left(22.50 - 1.187 * 10^{-2}\frac{T}{K}\right) dT\; J = 3.79\; kJ$

The Cv part is much bigger (the numbers in example 3.5 are bit different since Cv approximation is better). One can mostly ignore the $\frac{\partial U}{\partial V}$ part.

Dependence of Enthalpy on T at constant P   Engel & Reid chapter 3.4

The enthalpy can be treated in similar way as U. Here we use the variables T and P

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

As discussed before

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

and in this system the P is constant so dP = 0.

$$\Delta H = \int_{T_1}^{T_2} C_P(T)\, dT$$

Go through example 3.6.

Note that the C_P model of graphite is quite complex, but it is needed because the C_P is not constant in the range of 300 to 600 K. With constant C_P the ΔH = 30.8 kJ and with the better model 46.9 kJ. Rather large difference. In most cases the constant Cp model is OK.

# Relation of C_P and C_V Engel & Reid chapter 3.5

We note earlier that for ideal gas the $C_P - C_V$ = nR but the more general relations if more complex.

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = C_V + TV\frac{\beta^2}{\kappa}$$

Pressure gauges

$P_1 V_1 T_1$

Porous plug

$P_2 V_2 T_2$

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The Joule-Thomson experiment is a convenient way to measure the non-ideality of gases. In this experiment gas, originally at P_1, V_1, T_1 will be pressed through a porous membrane and at the end the P, T and V are P_2, V_2, T_2. The cylinder is isolated. P_1 is usually larger than P_2. The porous membrane is needed to make the process slow.
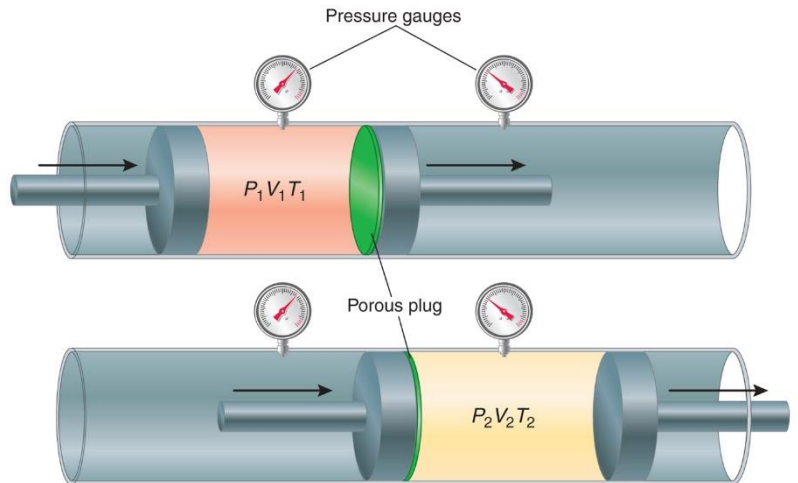
The work done is

$$w = w_{left} + w_{right} = -\int_{V_1}^{0} P_1 dV - \int_{0}^{V_2} P_2 dV = P_1 V_1 - P_2 V_2$$

The system is insulated so q=0 and $\Delta U = U_2 - U_1 = w = P_1 V_1 - P_2 V_2$ this can be rearranged as $U_1 + P_1 V_1 = U_2 + P_2 V_2 \implies H_1 = H_2$ so the enthalpy do not change. We are interested of the $\Delta T / \Delta P$. For real gases this is not zero. We can define the Joule-Thomson coefficient as

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H$$

the coefficient can be positive or negative. See table 3.3. We can also get the enthalpy pressure relation using the J-T coefficient. For isoenthalpic process

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

and

$$C_P \left(\frac{\partial T}{\partial P}\right)_H + \left(\frac{\partial H}{\partial P}\right)_T = 0 \implies \left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{J-T}$$

TABLE 3.3 Joule-Thomson Coefficients for Selected Substances at 273 K and 1 atm

Gas	μ_{J-T} (K/MPa)
Ar	3.66
C_6H_{14}	−0.39
CH_4	4.38
CO_2	10.9
H_2	−0.34
He	−0.62
N_2	2.15
Ne	−0.30
NH_3	28.2
O_2	2.69

Source: Linstrom, P. J., and Mallard, W. G., eds. NIST Chemistry Webbook: NIST Standard Reference Database Number 69. Gaithersburg, MD: National Institute of Standards and Technology. Retrieved from http://webbook.nist.gov.

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Thermochemistry is an important part of chemistry. It connects the thermodynamics to chemical reactions. Thermochemistry and reaction kinetics are essential tools for understanding the chemical reactions. We will discuss the kinetics later. In any chemical reaction, each compound has well defined enthalpy if the reaction happens in constant pressure.

Example: ammonia forming in gas phase $\frac{1}{2}$ N_2(g) + 3/2 H_2(g) -> NH_3(g)
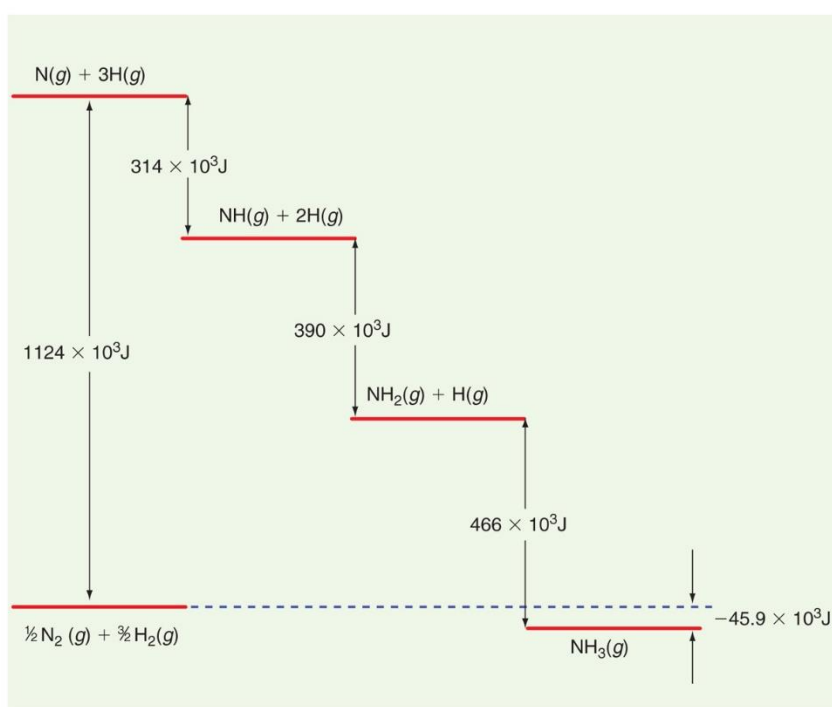
The total reaction enthalpy change is quite small, -46 kJ/mol but it is very difficult to break the N_2 molecule. In reality, this reaction does not happen in gas phase. It needs some catalyst. The thermochemistry is not restricted to gas phase. The reaction can happen in solution, in solid material or on surface.

When tabulating the reaction enthalpy values the pressure is set to 1 atm, the temperature to 298.15 K (25 °C) and amount of material is 1 mol. This is called **the standard enthalpy of reaction**, ΔH_R^o. The reaction enthalpy is the difference of product and reactant enthalpies

$$\Delta H_R^o = H_{prod}^o - H_{react}^o$$

The reaction enthalpies are very useful quantities but there are so many reactions that they are not convenient to list. We can define standard enthalpy of formation ΔH_f^o. We choose for 1 mol of **pure** material at its most stable form the $\Delta H_f^o = 0$. See **Tables 4.1 and 4.2**.

This needs an example: reaction $Fe_3O_4(s) + 4H_2(g) -> 3Fe(s) + 4H_2O(l)$

here H_2 is in it most stable form, so $\Delta H_f^o(H_2, g) = 0$, and $\Delta H_f^o(O_2, g) = 0$ the formation enthalpy of liquid water is

$$\Delta H_f^o(H_2O, l) = H_m^o(H_2O, l) - H_m^o(H_2, g) - \frac{1}{2}H_m^o(O_2, g) = -285.8 \; kJ/mol$$

and the formation enthalpy of Fe_3O_4 is

$$\Delta H_f^o(Fe_3O_4, s) = H_m^o(Fe_3O_4, s) - H_m^o(Fe, s) - 2H_m^o(O_2, g) = -1118.4 \; kJ/mol$$

where $H_m^o(Fe, s) = 0$ and $H_m^o(O_2, g) = 0$ then $\Delta H_f^o(Fe_3O_4, s) = H_m^o(Fe_3O_4, s)$.

the reaction enthalpy is

$$\Delta H_R^o = 4\Delta H_f^o(H_2O, l) - \Delta H_f^o(Fe_3O_4, s)$$

Is this positive or negative ? (-4*285.8 + 1118.4)kJ/mol = -24.8 kJ/mol)

In more general reaction

$$v_A A + v_B B .. \rightarrow v_X X + v_Y Y ..$$
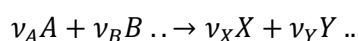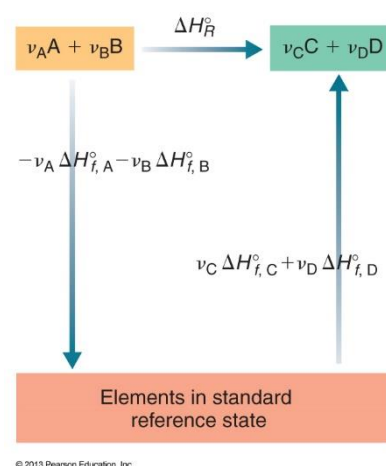
the reaction enthalpy is

$$\Delta H_R^o = \sum_i v_i H_f^o(i), \text{ where } \sum_i v_i = 0$$

we still have quite many enthalpies in the equations above. Note that the molar enthalpies of pure substances in its most stable form to 0.
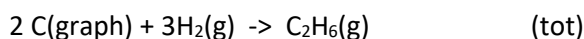
See Table 4.1 and 4.2

What is the formation enthalpy of diamond?

| Hess's law | Engel & Reid chapter 4.3 |

Even most of the pure substances enthalpies are known sometimes it is convenient to use other reaction and their enthalpies

$$2 \; C(graph) + 3H_2(g) \; -> \; C_2H_6(g) \qquad (tot)$$

one can also use the following oxidation reactions

$$C_2H_6(g) + 7/2 \; O_2(g) \; -> \; 2CO_2(g) + 3H_2O(g) \quad \Delta H_I^o \qquad (1)$$

$$C(graph) + O_2(g) \qquad -> \; 2CO_2(g) \qquad\qquad \Delta H_{II}^o \qquad (2)$$

$$H_2(g) + \tfrac{1}{2} \; O_2(g) \qquad -> \; H_2O(g) \qquad\qquad \Delta H_{III}^o \qquad (3)$$
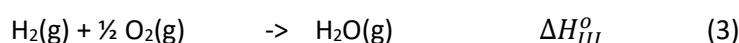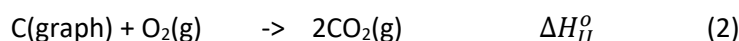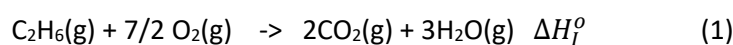
the reaction (tot) can also be written as 2*(2) –(1)+3*(3)

Exercise: From table 4.1 and 4.2 what are the enthalpies ΔH_I^o, ΔH_{II}^o and ΔH_{III}^o

Go through example 4.1

There is a quiz of this. (What is the OH bond enthalpy of OH(g)?)

The average OH bond enthalpy of water is 463.5 kJ/mol and the average bond energy is 461 kJ/mol.

Why the difference is so small.

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,0.98 105 --- 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,3.44 142 494 459 142,494 190	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,2.19 ≈220 ---,481 322 335,544 490	S,2.58 240 425 363 ---,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 ---,380 247 301,389 ≈440	Se,2.55 172 272 276 --- ≈351	Br,2.96 190 --- 362 201 250	Kr 50
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 84 ≈131
Cs,0.79 44 --- 176 --- 502	Ba,0.89 44 --- --- 467,561 578	Tl,2.04 100 --- --- --- 439	Pb,2.33 --- --- --- --- ≈360	Bi,2.02 --- ---,192 --- ≈350	Po,2.00 116	At,2.20	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

Examine Table 4.3

What are the bond energies of HF, FF, HC, HN, HO bonds. Is N_2 more stable than O_2 ? Note: what is the bond order in N_2 and O_2.

We can estimate the enthalpies from this table but it is better to use the table 4.2 and 4.3 values. They are more accurate.

Temperature dependence of reaction enthalpy
Engel & Reid chapter 4.4

The standard conditions are 1 atm pressure and room temperature but how to compute the reaction enthalpies at other temperatures. We can use the heat capacity.

$$\Delta H_R^o(T) = \Delta H_R^o(T = 298.15K) + \int_{T_1}^{T} C_P(T') \, dT'$$

Go through example 4.2

Note that in this example the temperature dependence of heat capacity is taken into account. If this is not known we can assume that the C_P is constant (and it is listed in table 4.1 and 4.2).

Calorimeter is a device that can be used to determine enthalpies. A simple example is the measurement of dissociation enthalpies of salts. We can add know amount of salt to water and measure the temperature change of the surrounding water. The whole system needs to be thermally insulated from the environment. The top cap of the container is not tight, so the system is in constant pressure (so we measure the enthalpy).

$$\Delta H = n_s\Delta H_{react} + n_{water}C_{P,m}(wat)\Delta T + C_{calor}\Delta T = 0$$

The bomb calorimeter (tight top cap and strong container -> constant V) can be used to measure combustion (=oxidation) internal energies.

$$\Delta U = n_s\Delta U_{react} + n_{water}C_{V,m}(wat)\Delta T + C_{calor}\Delta T = 0$$

Go through example 4.3

We need the heat capacity of the calorimeter. In the process both water and calorimeter will warm up. Any reaction with known reaction enthalpy can be used as reference. Here the is combustion of cyclohexane is used as reference. 0.972 g of c-hex will heat the water 2.98 C. There is 1.812 kg of water and $C_{P,m}(wat)$ = 75.3 J/(K mol). The c-hex combustion energy is -3913 kJ/mol.

The C_{calor} = 7.59 kJ/K

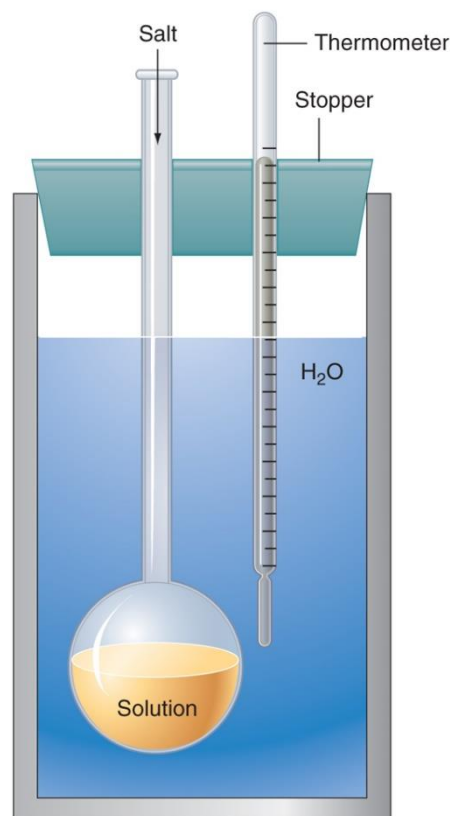if 0.872 g of benzene will heat the water 2.36 C, what is the combustion energy.

U(benzene) = -3260 kJ/mol.

Go through example 4.4

This is like example 4.3. The calorimeter constant is the heat capacity of the calorimeter.

Examples

The combustion enthalpy of benzene is -3268 kJ/mol and for cyclohexane -3920 kJ/mol. Why they are different?

Hint: wrote the reaction equations.

Find from Table 4.2 the combustion enthalpy of ethanol. Why it is smaller than the benzene one?

The density of these liquids is roughly the same (see Table 2.4). Is ethanol less effective fuel than benzene? Make a rough estimate of how many moles there are in 1 L of liquid and multiply this with the combustion enthalpy.

Sugars are an important energy form for animals. Find the combustion enthalpy of glucose and sucrose. Compare the enthalpy of glucose to hexane.

Fatty acids are long hydrocarbon chains with acid groups. Examples: Palmitate $CH_3(CH_2)_{14}COO-$, Behenate $CH_3(CH_2)_{20}COO-$ and linoleate $CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COO-$.

Why the fatty acids contain more energy than sugars?

Compare the combustion enthalpies of sugars and hydrocarbons. Note: in cells (in body) these molecules are fully oxidated but the reactions are complex (several steps and catalysed by enzymes).

In human the fatty acids can produce ca. 6 time more energy than sugars (per weight).

Chapter 4.6 is not discussed here, but if you have time try to read it.