

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  $\kappa$  and isobaric volumetric thermal expansion coefficients  $\beta$  as

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

These can be measured experimentally and some values 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

$$dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV$$

Go through example 3.1 (a bit boring math but useful)

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

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

and

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

For the size of the two terms for internal energy of N<sub>2</sub> **go through example 3.6.**

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

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

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

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

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  
Reid chapter 3.4

Engel &

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 3.7.

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  $\Delta H = 30.8$  kJ and with the better model 46.9 kJ. Rather large difference. In most cases the constant  $C_P$  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.

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

Joule-Thomson experiment

Engel & Reid chapter 3.7

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

$$\begin{aligned} w &= w_{left} + w_{right} \\ &= - \int_{V_1}^0 P_1 dV - \int_0^{V_2} P_2 dV \\ &= P_1 V_1 - P_2 V_2 \end{aligned}$$

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  $U_1 + P_1 V_1 = U_2 + P_2 V_2 \Rightarrow H_1 = H_2$  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

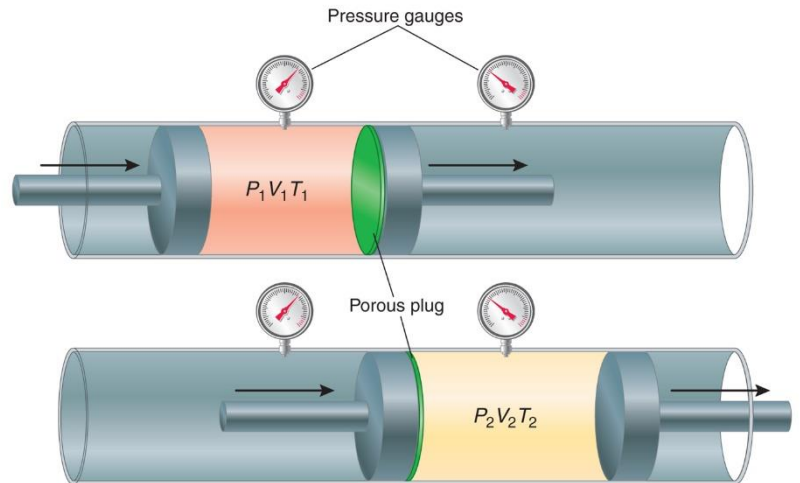
$$\mu_{J-T} = \left( \frac{\partial T}{\partial P} \right)_H$$

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

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



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

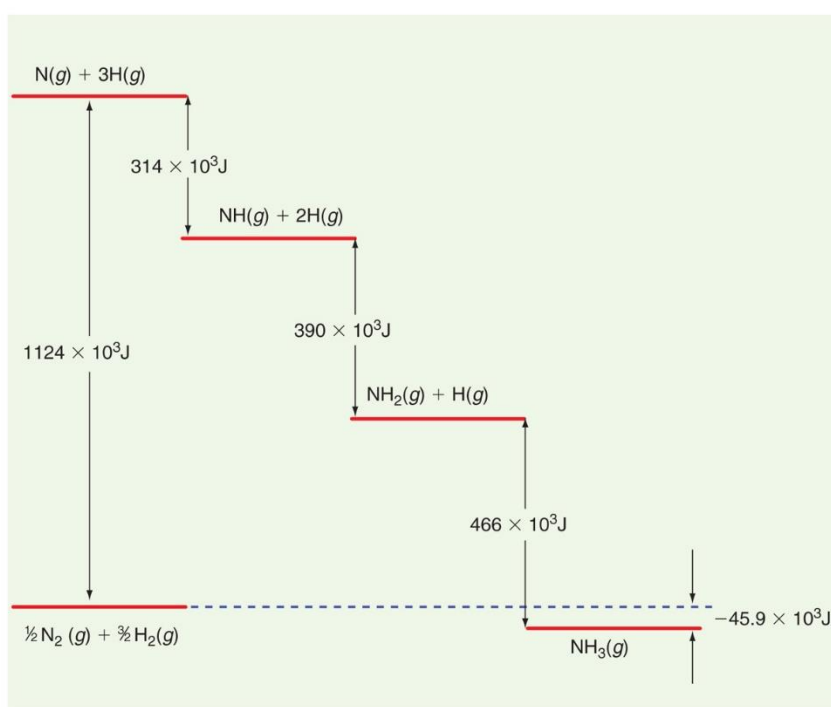
Gas	$\mu_{J-T}$ (K/MPa)
Ar	3.66
$C_6H_{14}$	-0.39
$CH_4$	4.38
$CO_2$	10.9
$H_2$	-0.34
He	-0.62
$N_2$	2.15
Ne	-0.30
$NH_3$	28.2
$O_2$	2.69

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  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$



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The total reaction enthalpy change is quite small, -46 kJ/mol but it is very difficult to break the  $\text{N}_2$  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**,  $\Delta H_R^\circ$ . The reaction enthalpy is the difference of product and reactant enthalpies

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

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  $\Delta H_f^\circ$ . **We choose for 1 mol of pure material at its most stable form the  $\Delta H_f^\circ = 0$ .** See **Tables 4.1 and 4.2.**

This needs an example: reaction  $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{l})$

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

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

and the formation enthalpy of  $Fe_3O_4$  is

$$\Delta H_f^\circ(Fe_3O_4, s) = H_m^\circ(Fe_3O_4, s) - H_m^\circ(Fe, s) - 2H_m^\circ(O_2, g) = -1118.4 \text{ kJ/mol}$$

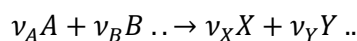
where  $H_m^\circ(Fe, s) = 0$  and  $H_m^\circ(O_2, g) = 0$  then  $\Delta H_f^\circ(Fe_3O_4, s) = H_m^\circ(Fe_3O_4, s)$ .

the reaction enthalpy is

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

Is this positive or negative ?

In more general reaction



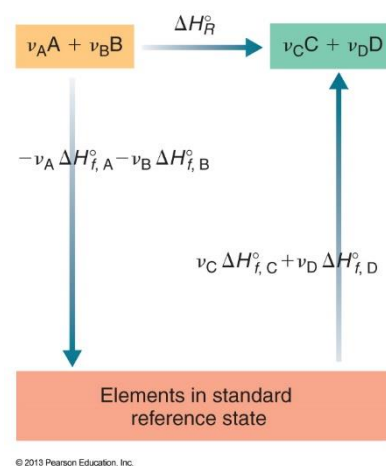
the reaction enthalpy is

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

we still have quite many enthalpies in the equations above. Note that the molar enthalpies of pure substances in their most stable form are 0.

See Table 4.1 and 4.2

What is the formation enthalpy of diamond?

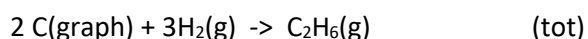


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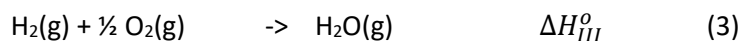
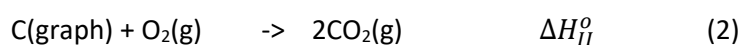
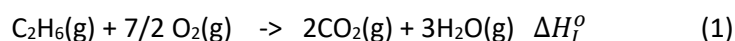
## Hess's law

## 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



one can also use the following oxidation reactions



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  $\Delta H_f^\circ$ ,  $\Delta H_{II}^\circ$  and  $\Delta H_{III}^\circ$

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**

1		2		Selected Bond Energies (kJ/mol)		13	14	15	16	17	18
<b>H</b> , 2.20 432 --- 432 459 565											<b>He</b>
<b>Li</b> , 0.98 105 --- 243 573		<b>Be</b> , 1.57 208 --- ---, 444 632				<b>B</b> , 2.04 293 --- 389 536,636 613	<b>C</b> , 2.55 346 602,835 411 358,799 485	<b>N</b> , 3.04 167 418,942 386 201,607 283	<b>O</b> , 3.44 142 494 459 142,494 190	<b>F</b> , 3.98 155 --- 565 ---	<b>Ne</b>
<b>Na</b> , 0.93 72 --- 197 477		<b>Mg</b> , 1.31 129 --- ---, 377 513				<b>Al</b> , 1.61 --- 272 583	<b>Si</b> , 1.90 222 318 318 452,640 565	<b>P</b> , 2.19 ≈220 ---, 481 322 335,544 490	<b>S</b> , 2.58 240 425 363 ---, 523 284	<b>Cl</b> , 3.16 240 --- 428 218 249	<b>Ar</b>
<b>K</b> , 0.82 49 --- 180 490		<b>Sr</b> , 1.00 105 --- ---, 460 550				<b>Ga</b> , 1.81 113 --- ---	<b>Ge</b> , 2.01 188 272 ---	<b>As</b> , 2.18 146 ---, 380 247 301,389 =440	<b>Se</b> , 2.55 172 272 276 --- =351	<b>Br</b> , 2.96 190 --- 362 201 250	<b>Kr</b> 50
<b>Rb</b> , 0.82 45 --- 163 490		<b>Sr</b> , 0.95 84 --- ---, 347 553				<b>In</b> , 1.78 100 --- ---	<b>Sn</b> , 1.80 146 --- ---	<b>Sb</b> , 2.05 121 ---, 295 ---	<b>Te</b> , 2.10 126 218 238 ---	<b>I</b> , 2.66 149 --- 295 201 278	<b>Xe</b> 84 ≈131
<b>Cs</b> , 0.79 44 --- 176 502		<b>Ba</b> , 0.89 44 --- 467,561 578				<b>Tl</b> , 2.04 --- --- ---	<b>Pb</b> , 2.33 --- --- ---	<b>Bi</b> , 2.02 --- ---, 192 =350	<b>Po</b> , 2.00	<b>At</b> , 2.20 116	<b>Rn</b>

**KEY**

Element symbol	<b>C</b> , 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

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Examine Table 4.3

What are the bond energies of HF, FF, HC, HN, HO bonds. Is N<sub>2</sub> more stable than O<sub>2</sub>? Note: what is the bond order in N<sub>2</sub> and O<sub>2</sub>.

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

## Engel & Reid chapter 4.5

Calorimeter is a device that can be used to determine the 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 need to be 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).

The bomb calorimeter (constant V) can be used to measure combustion (=oxidation) internal energies.

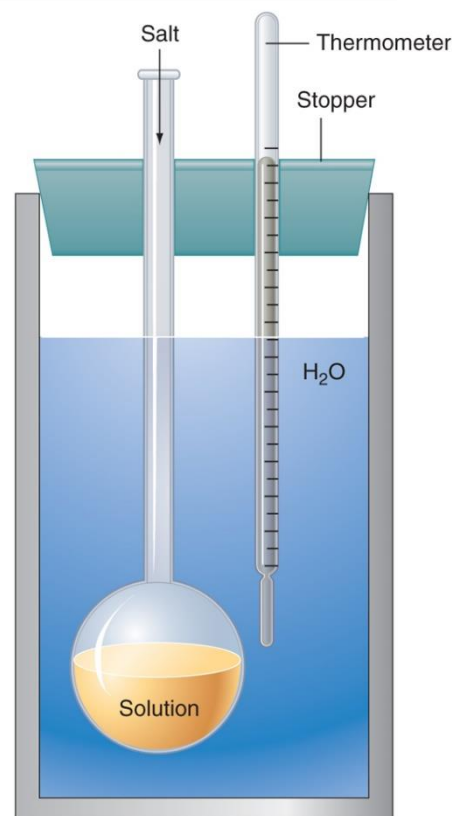
$$\Delta U = n_s \Delta U_{react} + n_{water} C_{P,m}(wat) \Delta T + C_{P,calor} \Delta T = 0$$

Go through example 4.3

We need the heat capacity of the calorimeter. The reference reaction is combustion of cyclohexane. 0.972 g of c-hex will head the water 2.98 C. There is 1.812 kg of water and  $C_{P,m}(wat) = 75.3 \text{ J}/(\text{K mol})$ . The c-hex combustion energy is -3913 kJ/mol.

The  $C_{P,calor} = 7.59 \text{ kJ}/\text{K}$

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





$U(\text{benzene}) = -3260 \text{ kJ/mol}$ .

The combustion enthalpy of benzene is  $-3268 \text{ kJ/mol}$  and for cyclohexane  $-3920 \text{ kJ/mol}$ . Why they differ?

Hint: wrote the reaction equations.

There is a quiz of this.

Find from the 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.

There is a quiz of this.

Go through example 4.4

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

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