2. ENTHALPY AND SPECIFIC HEAT CAPACITY

In this chapter, definition of enthalpy is discussed for a chemically reacting substance, whose thermodynamic state is defined by the equation

$$h = h(T,p) \tag{2.1}$$

at a temperature of T and pressure p. When defining the enthalpy of real gases and real liquid mixtures, the mole amounts of different components have to be taken into account.

Enthalpy according to equation (2.1) is called specific enthalpy, i.e. its dimension is J/mol or J/kg depending on whether considering the mole amount 1 mol or the mass 1 kg. The same notion applies also for thermodynamic quantities, specific volume $v=v(T,p)$, specific internal energy u (J/mol or J/kg), specific entropy s (J/mol K or J/kgK), specific heat capacity at constant pressure c_p (J/mol K or J/kgK) and specific heat capacity in constant volume c_v (J/mol K or J/kgK). Every equation presented after this are exactly the same regardless of choice of molar or mass based specific quantities[*)].

2.1 Definitions

Specific heat capacity c_p is defined with the equation

$$c_p \equiv \left(\frac{\partial h}{\partial T} \right)_p . \tag{2.2}$$

Equations (2.1) and (2.2) result in

$$c_p = c_p \, (T,p). \tag{2.3}$$

Specific volume v is similarly dependent on temperature and pressure

$$v = v \, (T,p). \tag{2.4}$$

Equation (2.4) is called the equation of state for a substance. Based on the equation of state, the volumetric thermal expansion coefficient γ can be defined as

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[*)] The connection between a molar based specific quantity g_{mol} (g = u,h,v,s,c_p,c_v,...) and a mass based specific quantity g_{mas} is $g_{mol} = M \, g_{mas}$, where M is the molar mass of the substance (kg/mol).

$$\gamma \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad (2.5)$$

and the isothermal compressibility factor κ_T as

$$\kappa_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T. \qquad (2.6)$$

Note that $\gamma = \gamma(T,p)$ and $\kappa_T = \kappa_T(T,p)$.

Example 2.1. The specific molar volume of an ideal gas is

$$v = \frac{V}{n}.$$

Inserting the ideal gas law pV=nRT to this results in

$$v = v(T,p) = \frac{RT}{p},$$

where it can be seen that the specific molar volume of an ideal gas is the same for every gas.

For an ideal gas, the equation (2.5) results in

$$\gamma = \frac{1}{v}\frac{\partial v}{\partial T} = \frac{1}{v}\frac{R}{p} = \frac{1}{v}\frac{1}{T}\frac{RT}{p} = \frac{1}{v}\frac{1}{T}v = \frac{1}{T}$$

and accordingly, for an ideal gas, the equation (2.6) results in

$$\kappa_T = -\frac{1}{v}\frac{\partial v}{\partial p} = -\frac{1}{v}\frac{-RT}{p^2} = \frac{1}{v}\frac{1}{p}\frac{RT}{p} = \frac{1}{p}.$$

For enthalpy change with respect to pressure, an equation can be derived [2]

$$\frac{\partial h}{\partial p} = v - T\left(\frac{\partial v}{\partial T}\right)_p, \qquad (2.7)$$

which can be written with the volumetric thermal expansion coefficient equation (2.5) as

$$\frac{\partial h}{\partial p} = v(1 - T\gamma) .$$ (2.8)

The following applies for the total differential of enthalpy h=h(T,p)

$$dh = \frac{\partial h}{\partial T} dT + \frac{\partial h}{\partial p} dp ,$$

with equations (2.2) and (2.8) this becomes

$$dh = c_p dT + v(1 - T\gamma)dp .$$ (2.9)

Integrating equation (2.9) results in

$$h(T, p) - h(T_o, p_o) =$$

$$= \int_{T_o}^{T} c_p (T, p_o) dT + \int_{p_o}^{p} v(T, p)(1 - T\gamma (T, p))dp$$ (2.10)

In order to calculate enthalpy changes compared to a known state (T_O, p_O), the function $c_p(T,p_O)$ has to be known, which is the specific heat capacity as a function of temperature at pressure p_O, as well as the equation of state (2.4), which results in the volumetric thermal expansion coefficient $\gamma (T,p)$ by applying the equation (2.5).

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Example 2.2. For an ideal gas $\gamma (T,p) = 1/T$ and the equation (2.8) results in $(\partial h / \partial p)_T = 0$, meaning that

$$h (T,p) = h(T).$$

Generally, gases are closer to an ideal gas the lower the pressure p is. For example, air at a pressure of 1 bar can be considered as an ideal gas with reasonable accuracy, but at higher pressures the deviation becomes significant.

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2.2 Reaction enthalpy

Enthalpy change

$$\Delta H \equiv H(B) - H(A)$$ (2.11)

from state A = $(T, p, n_1, n_2, ..., n_m)$ to state B = $(T, p, n'_1, n'_2, ..., n'_m)$ is called <u>reaction enthalpy,</u> when temperatures and pressures are equal in the initial state (A) and the final state (B).

When the reaction enthalpy $\Delta H < 0$, the reaction is <u>exothermic,</u> and heat is released. If $\Delta H > 0$, the reaction is <u>endothermic,</u> and heat is absorbed. If the reaction takes place in a thermally insulated container, an endothermic reaction lowers the temperature and an exothermic reaction increases it.

Example 2.3. Let's consider the combustion reaction of carbon

$$C(s) + O_2(g) \rightarrow CO_2(g). \qquad (2.12)$$

At the initial state of the process A the reactants carbon $C(s)$ and oxygen $O_2(g)$ are not yet reacting. At the final state of the process B carbon and oxygen have reacted and formed carbon dioxide.

When the initial and final states of the combustion reaction are at the standard state $T = 298.15$ K and $p = 1.0$ bar, the reaction enthalpy becomes

$$\Delta H = \Delta H^o = H(B) - H(A) = -393.5 \text{ kJ/mol},$$

where mole corresponds to the number of gross reactions according to the combustion reaction equation, which in this case is the same as the amount of carbon $C(s)$ or oxygen $O_2(g)$ consumed or carbon dioxide $CO_2(g)$ formed during the reaction in moles. Therefore, the number of these written reactions occurring is equal to one mole, i.e. the Avogadro number $6.023 \cdot 10^{23}$[*). The enthalpy at the initial state is $H(A) = H(C(s)) + H(O_2(g))$ and at the final state $H(B) = H(CO_2(g))$. The notation ΔH^o means that the reaction enthalpy is defined at the standard state.

Example 2.4. The gross reaction of combustion of propane gas is

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$$
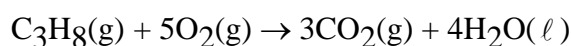
and the stated reaction enthalpy at the standard state is $\Delta H^o(298.15K) = -2220$ kJ/mol. The mole corresponds to the number of gross reactions according to the equation above, which in this case is equal to the amount of combusted propane gas $C_3H_8(g)$ in moles.

[*) A mole is equal to the Avogadro number, i.e. $1 \text{ mol} \equiv 6.023 \cdot 10^{23}$. It is therefore an abbreviation quantity similar to for example million.

2.3 Enthalpy of formation

The combustion reaction of carbon $C(s) + O_2(g) \rightarrow CO_2(g)$ is an example of a formation reaction for carbon dioxide. Enthalpy of formation of a chemical compound ΔH_f° is the enthalpy change between the compound at the standard state and its reference state, where its elements are in a stable form. The enthalpy of formation is dependent on temperature: $\Delta H_f^\circ(T)$. The lower index f denotes the word formation. For example, the enthalpy of formation of liquid water at the standard state (table 2.1) at a temperature of 25 °C is $\Delta H_f^O(l;298.15 \text{ K}) = -285.830$ kJ/mol and accordingly, the enthalpy of formation of water vapor at the same temperature is $\Delta H_f^O(g;298.15 \text{ K}) = -241.826$ kJ/mol (table 2.1 or table 1.1). According to the definition, the enthalpy of formation at the reference state is zero, for example $\Delta H_f^\circ(O_2(g)) = 0$.

The enthalpy of formation of a compound depicts the total amount of energy absorbed or released to the environment by a process occurring at constant temperature and pressure. If ΔH_f° is positive, energy is required to form the compound.

Table 2.1. Enthalpies of formation for a selection of substances [3] at the standard state (p = 100 kPa) at a temperature of T = 298.15 K.

	ΔH_f° (MJ/kmol)		ΔH_f° (MJ/kmol)
$CO_2(g)$	-393.505	$SO_2(g)$	-296.813
$CO(g)$	-110.541	$SO_3(g)$	-395.765
$H_2O(g)$	-241.826	$NO(g)$	90.291
$H_2O(l)$	-285.830	$NO_2(g)$	33.095
$CH_4(g)$	-74.873	$N_2O(g)$	82.048
$C_2H_6(g)$	-84.684	$NH_3(g)$	-45.940
$C_3H_8(g)$	-103.847	$HCN(g)$	-135.143
$C_4H_{10}(g)$	-126.148	CaO	-635.089
$H_2S(g)$	-20.502	$CaCO_3(calcite)$	-1206.921
$COS(g)$	-138.407	$Ca(OH)_2$	-986.085

The enthalpy $h(T,p)$ (J/mol) of gases, pure solid substance and pure liquid at the standard state is denoted as $h^\circ(T)$ [often in tables as $H^\circ(T)$]. Its value at the starting point of an enthalpy scale $(T_o, p_o = p^o)$ is defined as the value of enthalpy of formation

$$h^\circ(T_o) \equiv h(T_o, p_o) \equiv \Delta H_f^\circ(T_o).$$ (2.13)

When using the enthalpy scale agreement 1° presented in section 1.3, a common agreement is that $T_o = 298.15$ K.

The deeper meaning of equation (2.13) is that by using enthalpies of formation the composing of impossible absolute internal energy and enthalpy scales can be avoided. This is proven in the following example where the reaction enthalpy of the combustion of propane gas is defined with the enthalpies of formation. In other words, the example shows why enthalpies based on the definition (2.13) yield correct values of enthalpies of reaction.

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Example 2.5. For the reaction

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$$
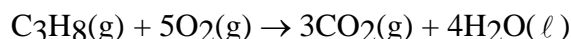
the reaction enthalpy at the standard state at a temperature of T according to the definition is

$$\Delta H^o = [3\,h^o(CO_2(g)) + 4\,h^o(H_2O(\ell))] - h^o(C_3H_8(g)) + 5\,h^o(O_2(g))],$$

where quantities $h^o(CO_2(g)),..., h^o(O_2(g))$ depict the enthalpies of the components at the standard state expressed with a physically correct common energy scale. We can assume that such scale exists or that at least in principle such a scale can be composed.

The expression of reaction enthalpy can be written in the following equivalent form

$$\Delta H^o = [3\{h^o(CO_2(g)) - h^o(C(s)) - h^o(O_2(g))\} + 4\{h^o(H_2O(l)) -$$
$$h^o(H_2(g)) - 1/2\ h^o(O_2(g))\}] - [\{h^o(C_3H_8(g)) - 3\,h^o(C(s)) -$$
$$4\,h^o(H_2(g))\} + 5\{h^o(O_2(g)) - h^o(O_2(g))\}],$$

since the enthalpy terms $h^o(C(s))$, $h^o(O_2(g))$ ja $h^o(H_2(g))$ of the elements present in the equation balance each other out. On the other hand, the expressions in round brackets in the equation are exactly the same as the enthalpies of formation of the compounds:

$$\Delta H_f^o(CO_2(g)) = h^o(CO_2(g)) - h^o(C(s)) - h^o(O_2(g))$$
$$\Delta H_f^o(H_2O(l)) = h^o(H_2O(l)) - h^o(H_2(g)) - 1/2\ h^o(O_2(g))$$
$$\Delta H_f^o(C_3H_8(g)) = h^o(C_3H_8(g)) - 3\,h^o(C(s)) - 4\,h^o(H_2(g))$$
$$\Delta H_f^o(O_2(g)) = h^o(O_2(g)) - h^o(O_2(g)).$$

When both the reactants and the products are at the standard state at a temperature of T, the equation can be written as

$$\Delta H^o = 3\,\Delta H_f^o(CO_2(g)) + 4\,\Delta H_f^o(H_2O(l)) - \Delta H_f^o(C_3H_8(g))$$
$$- 5\,\Delta H_f^o(O_2(g))$$

and with enthalpies according to the enthalpy scale agreement 2° ($T_o{=}T$) and the definition (2.13), $\Delta H^o = 3\,h^o[CO_2(g)] + 4\,h^o[H_2O(l)] - h^o[C_3H_8(g)] - 5\,h^o[O_2(g)]$, which proves the usefulness of the definition (2.13).

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Was it a pure coincidence that the decomposition done in the example, which was used to form enthalpies of formation in the round brackets, is identical with the reaction equation? No. By decomposing the elements of each compound it can be always shown that the element terms cancel each other since there is an equal amount of moles on both sides of the reaction equation. This is a direct result of the element balance. A reaction equation is one way to represent element balance. When the enthalpies of the elements according to the mole amounts are reduced from the enthalpy terms, they cancel each other when calculating the enthalpy difference between the initial and final states according to the element balance, given that the temperatures are the same. This procedure is therefore universal when calculating the reaction enthalpy.

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Example 2.6. Let's calculate the reaction enthalpy of the combustion reaction of propane gas $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$ at $T{=}T_o = 298.15$ K using the enthalpies of formation:

$C_3H_8(g;\ 298.15\ K),\ \Delta H_f^o = -\ 103.8$ kJ/mol

$O_2(g;\ 298.15\ K),\ \Delta H_f^o = 0$

$CO_2(g;\ 298.15\ K),\ \Delta H_f^o = -\ 393.5$ kJ/mol

$H_2O(\ell;\ 298.15\ K),\ \Delta H_f^o = -\ 285.8$ kJ/mol

and therefore

$\Delta H^o(298.15\ K) = [3(-\ 393.5) + 4(-\ 285.8)] - [1(-\ 103.8) + 5 \cdot 0] =$
$= -\ 2220$ kJ/mol.

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When analyzing reactions where the temperatures at the initial and final states are not equal, the enthalpies of the compounds at different temperatures are needed. In this case, the enthalpy difference between reactants and products cannot be calculated as in examples 2.5-2.6 (enthalpy scale agreement 2°, section 1.3) only based on the

enthalpies of formation, even if they are known at different temperatures. In the next section, defining enthalpies according to the enthalpy scale agreement 1° is discussed.

2.4 Enthalpy scale agreement 1° for a chemically reacting compound

2.4.1 Temperature dependence of enthalpy and specific heat capacity

If the enthalpy of formation and specific heat capacity are known, the enthalpy at the standard state at a given temperature can be written according to equations (2.10) and (2.13) as

$$h(T, p^{o}) = h^{o}(T) = \Delta H_f^o (T_o) + \int_{T_0}^{T} c_p^o (T)dT. \tag{2.14}$$

where a notation $c_p(T,p^o) = c_p^o(T)$ is used. The equation (2.14) follows the enthalpy agreement 1° presented in section 1.3, according to which the starting point of the enthalpy scale is set at a temperature of T_o and at the starting point of the scale $h^o(T_o) = \Delta H_f^o (T_o)$.

In tables the integral term is often already calculated in the form

$$h^{o}(T) - h^{o}(T_o) \equiv \int_{T_0}^{T} c_p^o (T)dT,$$

which results in

$$h^{o}(T) = \Delta H_f^o (T_o) + [h^{o}(T) - h^{o}(T_o)]. \tag{2.15}$$

The term $[h^o(T)-h^o(T_o)]$ is called *sensible enthalpy* or *table enthalpy*. In chapter 12, where combustion is discussed, the table enthalpies of important gases related to combustion are presented.

In the case of a phase change from phase I to phase II at a temperature of T_{tr}, for example the liquification of a substance, the enthalpy change taking place during the phase change $\Delta H_{tr}°$ has to be added to equation (2.14):

$$h(T,p^o) = \Delta H_f^o(T_o) + \underbrace{\int_{T_o}^{T_{tr}} c_{p,I}^o(T)dT}_{\substack{temperature\ rise \\ of\ phase\ I\ T_o->T_{tr}}} + \underbrace{\Delta H_{tr}^o(T_{tr})}_{\substack{phase\ change \\ between\ phases \\ I\ and\ II}} + \underbrace{\int_{T_{tr}}^{T} c_{p,II}^o(T)dT}_{\substack{temperature\ rise \\ of\ phase\ II\ T_{tr}->T}}$$

$$(2.16)$$

Example 2.7. Aluminum oxide (α - Al_2O_3, crystal (delta)) is a heat resistant ceramic substance. Calculate its enthalpy at temperatures of 273.15 K and 1000 K.

The reference state of the compound is crystalline aluminum metal Al(cr) and oxygen gas O_2(g). From table 2.2 we can see at a temperature of T_0 = 298.15K (in Janaf tables T_o is denoted with the symbol T_r)

$$\Delta H°_f(T_O) = - 1666.487 \text{ kJ/mol.}$$

At a temperature of T_O = 298.15 K the specific heat capacity of aluminum oxide is

$$c_p(T_O) = 81.385 \text{ J mol}^{-1} \text{ K}^{-1}.$$

The enthalpy of aluminum oxide at a temperature of 273.15 K is according to equation (2.14)

$$h(T=273.15 \text{ K, } p°) = - 1666.487 + 81.385 \cdot 10^{-3} \cdot (273.15\text{-}298.15)$$
$$= - 1668.522 \text{ kJ/mol.}$$

Specific heat capacity c_p is highly dependent on the temperature. For example, for aluminum oxide at a temperature of 600 K it is c_p = 115.92 J mol^{-1} K^{-1}. Therefore, the enthalpy at 1000 K is best defined with a beforehand calculated tabulated integral based on equation (2.15). From the table we can easily see that

$$h^O(1000 \text{ K}) - h^O(T_o) = 80.304 \text{ kJ/mol } (T_O = 298.15 \text{ K})$$

and with equation (2.15) the enthalpy is

$$h(T = 1000 \text{ K, } p°) = - 1666.487 + 80.304 = - 1586.183 \text{ kJ/mol.}$$

Enthalpy per unit mass is accordingly

$$h(T = 1000 \text{ K, } p°) = -1586.183/0.10196 = - 15.56 \text{ MJ/kg,}$$

where $M_{Al_2O_3}$ = 0.10196 kg/mol.

Specific heat capacities c_p of gases at different temperatures are presented in table 2.3. For monatomic gases, so called noble gases, the specific heat capacity is independent on the temperature. For example, for argon gas c_p = 20.786 J/(molK).

In table 2.4 standard enthalpy values h^o(T) of gases at different temperatures based on the equation (2.14) are presented. When calculating the integral expression, the

Table 2.2. Aluminum oxide (α - Al$_2$O$_3$, crystal (delta)).

JANAF THERMOCHEMICAL TABLES

ALUMINUM OXIDE, DELTA (δ-Al$_2$O$_3$) CRYSTAL (DELTA) $M_r = 101.96128$

$S°(298.15 \text{ K}) = [50.6 \pm 4] \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = [-1653.9 \pm 4] \text{ kJ mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -1666.5 \pm 4 \text{ kJ mol}^{-1}$
$\Delta_{fus} H° = [93.3] \text{ kJ mol}^{-1}$

$T_{fus} = [2308] \text{ K}$

Aluminum Oxide, Delta (Al$_2$O$_3$)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa   Al$_2$O$_3$(cr)

T/K	C$_p°$	S°	-(G°-H°(T$_r$))/T	H°-H°(T$_r$)	Δ_fH°	Δ_fG°	Log K$_f$
	J K^{-1}mol^{-1}			kJ mol^{-1}			
0							
100							
200							
298.15	81.385	50.626	50.626	0.	-1666.487	-1572.974	275.579
300	81.799	51.131	50.628	0.151	-1666.507	-1572.394	273.778
400	98.968	77.231	54.070	9.264	-1666.867	-1540.932	201.225
500	109.315	100.518	61.079	19.719	-1666.286	-1509.504	157.697
600	115.922	121.073	69.400	31.004	-1665.192	-1478.248	128.693
700	120.434	139.300	78.109	42.834	-1663.938	-1447.188	107.991
800	123.739	155.608	86.793	55.050	-1662.889	-1416.311	92.476
900	126.314	170.338	95.273	67.558	-1661.571	-1385.582	80.417
1000	128.514	183.764	103.460	80.304	-1681.850	-1353.447	70.697
1100	130.406	196.103	111.329	93.251	-1680.516	-1320.670	62.713
1200	132.100	207.524	118.875	106.378	-1679.063	-1288.020	56.066
1300	133.630	218.159	126.108	119.666	-1677.500	-1255.496	50.446
1400	135.013	228.113	133.042	133.099	-1675.837	-1223.096	45.634
1500	136.258	237.471	139.696	146.664	-1674.084	-1190.819	41.468
1600	137.362	246.301	146.085	160.346	-1672.253	-1158.660	37.826
1700	138.336	254.658	152.228	174.132	-1670.355	-1126.618	34.617
1800	139.197	262.590	158.141	188.009	-1668.402	-1094.690	31.767
1900	139.973	270.137	163.838	201.988	-1666.402	-1062.872	29.220
2000	140.706	277.336	169.335	216.002	-1664.362	-1031.180	26.931
2100	141.438	284.218	174.643	230.109	-1662.283	-999.550	24.862
2200	142.171	290.815	179.774	244.289	-1660.165	-968.040	22.984
2300	142.904	297.131	184.741	258.543	-1658.008	-936.629	21.272
2400	143.636	303.248	189.552	272.870	-1655.810	-905.312	19.704
2500	144.412	309.128	194.219	287.272	-1653.570	-874.087	18.263
2600	145.188	314.806	198.748	301.752	-1651.285	-842.953	16.935
2700	146.007	320.301	203.149	316.311	-1648.952	-811.907	15.707
2800	146.868	325.626	207.428	330.954	-2234.367	-779.013	14.533
2900	147.817	330.797	211.594	345.688	-2229.729	-727.118	13.097
3000	148.808	335.824	215.651	360.519	-2225.023	-675.384	11.759

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α-Al$_2$O$_3$ (1) using $\Delta_t H°(978 \text{ K}) = -2.7\pm0.4$ kcal mol^{-1} for the irreversible process $\delta \rightarrow \alpha$. This yields $\Delta_f H°(298.15 \text{ K}) = -2.2$ kcal mol^{-1} based on our adopted functions. Yokokawa and Kleppa (2) determined $\Delta_f H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. DTA studies by Gani and McPherson (3) gave $\Delta_t H° = -2,810.5$ kcal mol^{-1}. Assuming T = -1400 K, we derive $\Delta_f H°(298.15 \text{ K}) = -1.9$ kcal mol^{-1}. This confirms the calometric result. Both samples of δ-Al$_2$O$_3$ had been obtained by rapid quenching from high temperature, one (2) from combustion of Al$_4$C$_3$ and the other (3) by a plasma method.

Heat Capacity and Entropy

C$_p°$ is assumed to be 3% larger than that of α-Al$_2$O$_3$ (1) by comparison with the observed values for γ-Al$_2$O$_3$ (1). S° is selected such that $\Delta_r G°(\delta \rightarrow \alpha)<0$ below T$_{fus}$ and $\Delta_r G°(\delta \rightarrow \alpha)>0$ at T<2400 K. Marchidan et al. (4) measured enthalpy data (573-1177 K) for a sample designated only as TA-600 alumina. They attributed a transition at ~993 K (720°C) to the irreversible process $\eta \rightarrow \delta$. This temperature corresponds roughly to processes designated as either (γ or η)→θ or γ→δ by Lippens and Steggerda (5). DTA data of Alevra et al. (6) showed an endotherm near 750°C subsequent to the dehydration of hydroxide samples; however, TGA data indicated that the resulting alumina still retained considerable water at this temperature. The enthalpy data (4, 1003-1177 K) are 4.7±0.3% larger than those of α-Al$_2$O$_3$ (1) and presumably correspond to an alumina containing a significant amount of water. The δ-Al$_2$O$_3$ used in $\Delta_t H°$ studies was presumably essentially anhydrous. Thus, we omit the enthalpy data (4) on the presumption that they are larger than those of our standard state which is anhydrous δ-Al$_2$O$_3$.

Phase Data

The stable crystalline form is corundum (α-alumina). Delta-alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied (5) due to their importance in adsorbents and catalysts. Lippens and Steggerda (5) summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. Mixtures of the closely related δ- and θ-aluminas are also formed by rapid cooling of droplets of molten alumina following their passage through a flame (7). There is some controversy (5) over the X-ray data and unit-cell dimensions of δ-Al$_2$O$_3$ formed by the two methods. Recent data (8) for δ-Al$_2$O$_3$ (5) suggest a similar controversy. Delta-alumina belongs to the "nearly anhydrous", high-temperature classification (5) based on the temperature of 600° to 900°C at which it forms during dehydration. The irreversible transitions $\delta \rightarrow \theta(\rightarrow \alpha)\cdot\alpha$ are thermally activated at temperatures of 800°-1050°C for the first step (5, 6) and ~1200°C for the final step (5).

Fusion Data

The hypothetical melting point of metastable δ-phase is calculated as the temperature at which $\Delta_r G°(\delta \rightarrow \alpha)=0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

References

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temperature dependence is taken into account with a power series according to the database of the HSC software. The starting point of the enthalpy scale in table 2.4 is $T_O = 298.15$ K.

The standard state of gases is defined according to the ideal gas state. Since the enthalpy of an ideal gas is not dependent on the pressure or the composition of the gas mixture, tabulated values of h^o (H^o in Janaf tables) correspond to values of enthalpy of ideal gases at any pressure other than the standard pressure p^o. The enthalpy of an ideal gas is also not dependent on the mole amounts in the mixture and therefore values of h^o can be used for the components of an ideal gas mixture.

These enthalpies are very convenient in calculations since they include the energy changes associated with reactions.

Table 2.3. Specific heat capacities c_p of gases.

T	T	CH4	C2H6	C3H8	C4H10	H2	CO	N2	Ar	O2	CO2	H2S	H2O	COS	NH3
C	K								J/(mol*K)						
25	298.15	34.96	52.39	73.46	98.25	28.88	29.11	29.11	20.78	29.15	37.46	34.17	33.56	41.71	35.54
26.85	300	35.07	52.87	74.19	98.83	28.88	29.11	29.11	20.78	29.17	37.53	34.19	33.57	41.79	35.60
76.85	350	38.10	63.85	90.77	113.34	29.03	29.22	29.15	20.78	29.75	39.40	34.86	33.92	43.75	37.27
126.85	400	41.09	72.17	103.17	126.15	29.13	29.39	29.25	20.78	30.30	41.14	35.60	34.31	45.53	38.93
176.85	450	44.03	78.91	113.10	137.82	29.20	29.61	29.41	20.78	30.81	42.77	36.39	34.76	47.14	40.57
226.85	500	46.91	84.65	121.44	148.63	29.26	29.88	29.62	20.78	31.29	44.28	37.23	35.25	48.60	42.18
276.85	550	49.72	89.70	128.72	158.75	29.31	30.17	29.87	20.78	31.75	45.68	38.09	35.77	49.92	43.76
326.85	600	52.47	94.27	135.24	168.29	29.36	30.49	30.15	20.78	32.17	46.98	38.97	36.32	51.11	45.32
376.85	650	55.14	98.46	141.19	177.29	29.41	30.82	30.45	20.78	32.57	48.19	39.87	36.90	52.18	46.84
426.85	700	57.72	102.37	146.69	185.80	29.48	31.16	30.76	20.78	32.95	49.31	40.76	37.49	53.14	48.33
476.85	750	60.23	106.04	151.84	193.85	29.56	31.50	31.08	20.78	33.30	50.34	41.64	38.11	54.00	49.78
526.85	800	62.64	109.52	156.69	201.46	29.65	31.85	31.40	20.78	33.63	51.29	42.50	38.73	54.77	51.19
576.85	850	64.97	112.83	161.29	208.64	29.76	32.18	31.72	20.78	33.94	52.17	43.35	39.36	55.47	52.57
626.85	900	67.20	115.99	165.67	215.40	29.89	32.51	32.04	20.78	34.22	52.97	44.17	40.00	56.09	53.90
676.85	950	69.34	119.02	169.84	221.75	30.04	32.83	32.35	20.78	34.50	53.71	44.97	40.64	56.65	55.19
726.85	1000	71.38	121.93	173.84	227.69	30.20	33.13	32.65	20.78	34.75	54.38	45.73	41.27	57.14	56.44
776.85	1050	73.33	124.72	177.67	233.24	30.37	33.42	32.94	20.78	34.99	55.00	46.46	41.90	57.59	57.65
826.85	1100	75.18	127.41	181.34	238.39	30.56	33.69	33.21	20.78	35.21	55.56	47.16	42.53	58.00	58.81
876.85	1150	76.94	129.99	184.86	243.14	30.76	33.94	33.48	20.78	35.42	56.08	47.82	43.14	58.36	59.93
926.85	1200	78.61	132.48	188.24	247.50	30.96	34.18	33.72	20.78	35.62	56.54	48.45	43.75	58.69	61.01
976.85	1250	80.18	134.87	191.48	251.46	31.18	34.40	33.95	20.78	35.80	56.97	49.05	44.34	58.99	62.04
1026.85	1300	81.66	137.17	194.60	255.04	31.40	34.61	34.17	20.78	35.98	57.35	49.61	44.92	59.26	63.03
1076.85	1350	83.06	139.38	197.58	258.23	31.62	34.79	34.37	20.78	36.15	57.70	50.13	45.48	59.51	63.98
1126.85	1400	84.36	141.51	200.43	261.04	31.85	34.97	34.55	20.78	36.30	58.02	50.62	46.03	59.74	64.89

Example 2.8. The combustion reaction of methane is

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
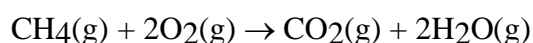
and its reaction enthalpy can be determined directly from table 2.4. Let's calculate its value at $T_O = 298.15$ K according to table 2.4:

$$\Delta H^o = h^o[CO_2] + 2h^o[H_2O] - h^o[CH_4] - 2h^o[O_2]$$

$$= -393.51 + 2 \cdot (-241.83) - (-74.87) - 2 \cdot 0$$

Table 2.4. Values of standard enthalpy $h^o(T)$ (kJ/mol) for different gases. Source: HSC.

T K	CH$_4$ metaani	C$_2$H$_6$ etaani	C$_3$H$_8$ propaani	C$_3$H$_8$ propeeni	C$_4$H$_{10}$ n-butaani	C$_4$H$_{10}$ iso-butaani	C$_4$H$_{10}$ 2-metyyli-propaani	CH$_3$OH metanoli	H$_2$ vety	CO hiili-monoksidi	CO$_2$ hiili-dioksidi
298.15	-74.87	-84.68	-103.93	-103.85	-126.15	-134.61	-134.73	-201.87	0.00	-110.54	-393.51
300	-74.81	-84.59	-103.79	-103.71	-125.97	-134.43	-134.55	-201.79	0.05	-110.49	-393.44
350	-72.97	-81.77	-99.80	-99.72	-120.70	-129.17	-129.69	-199.50	1.51	-109.02	-391.51
400	-70.98	-78.63	-95.29	-95.19	-114.80	-123.24	-124.82	-197.02	2.96	-107.55	-389.45
450	-68.85	-75.16	-90.30	-90.18	-108.30	-116.68	-119.96	-194.34	4.42	-106.08	-387.28
500	-66.58	-71.40	-84.86	-84.73	-101.22	-109.55	-115.10	-191.47	5.88	-104.59	-385.03
550	-64.16	-67.35	-78.99	-78.86	-93.60	-101.86	-110.23	-188.40	7.34	-103.08	-382.72
600	-61.61	-63.02	-72.72	-72.60	-85.46	-93.65	-105.37	-185.14	8.81	-101.57	-380.35
650	-58.93	-58.44	-66.08	-65.97	-76.83	-84.96	-100.51	-181.71	10.27	-100.04	-377.93
700	-56.11	-53.61	-59.08	-58.99	-67.74	-75.81	-95.64	-178.11	11.74	-98.50	-375.46
750	-53.17	-48.54	-51.75	-51.69	-58.22	-66.24	-90.78	-174.34	13.22	-96.94	-372.96
800	-50.10	-43.25	-44.11	-44.07	-48.30	-56.27	-85.91	-170.42	14.70	-95.37	-370.41
850	-46.92	-37.74	-36.18	-36.16	-38.01	-45.94	-81.05	-166.37	16.19	-93.78	-367.84
900	-43.62	-32.04	-27.98	-27.98	-27.38	-35.27	-76.19	-162.18	17.68	-92.19	-365.23
950	-40.22	-26.16	-19.54	-19.55	-16.44	-24.29	-71.32	-157.87	19.18	-90.57	-362.58
1000	-36.70	-20.10	-10.86	-10.87	-5.21	-13.03	-66.46	-153.45	20.69	-88.95	-359.91
1050	-33.09	-13.87	-1.98	-1.98	6.27	-1.52	-61.60	-148.94	22.21	-87.31	-357.22
1100	-29.38	-7.50	7.09	7.12	17.98	10.20	-56.73	-144.33	23.73	-85.66	-354.49
1150	-25.58	-0.99	16.32	16.41	29.88	22.12	-51.87	-139.65	25.26	-84.00	-351.74
1200	-21.69	5.64	25.70	25.87	41.94	34.21	-47.01	-134.90	26.81	-82.33	-348.97
1250	-17.71	12.39	35.20	35.48	54.15	46.42	-42.14	-130.09	28.36	-80.64	-346.17
1300	-13.66	19.24	44.81	45.23	66.45	58.75	-37.28	-125.24	29.92	-78.94	-343.35
1350	-9.53	26.18	54.50	55.10	78.84	71.15	-32.42	-120.36	31.50	-77.24	-340.51
1400	-5.34	33.20	64.26	65.07	91.28	83.59	-27.55	-115.45	33.08	-75.52	-337.65
1450	-1.08	40.28	74.06	75.13	103.73	96.06	-22.69	-110.53	34.67	-73.79	-334.78
1500	3.25	47.41	83.88	85.26	116.17	108.52	-17.83	-105.61	36.28	-72.05	-331.88

Table 2.4 (continued).

T / K	N_2 typpi	O_2 happi	Ar argon	H_2S rikkivety	H_2O vesi	COS karbonyyli-sulfidi	HCN vety-syanidi	NH_3 ammoni-akki	NO typpi-monoksidi	NO_2 typpi-dioksidi	SO_2 rikki-dioksidi	SO_3 rikki-trioksidi
298.15	0.00	0.00	0.00	-20.50	-241.83	-138.41	-135.14	-45.94	90.29	33.10	-296.81	-395.77
300	0.05	0.05	0.04	-20.44	-241.77	-138.33	-135.08	-45.87	90.35	33.16	-296.74	-395.67
350	1.51	1.53	1.08	-18.72	-240.08	-136.18	-133.23	-44.05	91.84	35.06	-294.70	-393.04
400	2.97	3.06	2.12	-16.98	-238.37	-133.90	-131.31	-42.16	93.34	37.06	-292.57	-390.25
450	4.44	4.62	3.16	-15.19	-236.65	-131.53	-129.31	-40.19	94.87	39.15	-290.36	-387.30
500	5.91	6.21	4.20	-13.36	-234.91	-129.09	-127.26	-38.14	96.41	41.30	-288.07	-384.20
550	7.39	7.81	5.24	-11.49	-233.13	-126.58	-125.15	-36.01	97.97	43.51	-285.70	-380.99
600	8.89	9.44	6.27	-9.58	-231.33	-124.03	-122.99	-33.81	99.54	45.78	-283.27	-377.66
650	10.41	11.08	7.31	-7.62	-229.50	-121.43	-120.79	-31.53	101.13	48.10	-280.79	-374.24
700	11.94	12.74	8.35	-5.62	-227.65	-118.79	-118.53	-29.17	102.73	50.46	-278.26	-370.75
750	13.48	14.40	9.39	-3.58	-225.76	-116.12	-116.23	-26.73	104.34	52.86	-275.69	-367.20
800	15.05	16.09	10.43	-1.49	-223.84	-113.41	-113.89	-24.21	105.97	55.30	-273.08	-363.59
850	16.63	17.78	11.47	0.63	-221.89	-110.67	-111.50	-21.61	107.61	57.78	-270.45	-359.92
900	18.22	19.48	12.51	2.79	-219.91	-107.90	-109.07	-18.94	109.26	60.29	-267.78	-356.22
950	19.84	21.19	13.55	4.99	-217.89	-105.11	-106.60	-16.20	110.93	62.84	-265.09	-352.47
1000	21.46	22.92	14.59	7.23	-215.84	-102.29	-104.10	-13.40	112.61	65.41	-262.38	-348.70
1050	23.10	24.65	15.63	9.51	-213.76	-99.45	-101.56	-10.54	114.30	68.02	-259.65	-344.89
1100	24.76	26.39	16.67	11.82	-211.65	-96.59	-99.00	-7.62	116.00	70.65	-256.90	-341.05
1150	26.43	28.15	17.71	14.16	-209.51	-93.70	-96.41	-4.65	117.71	73.30	-254.14	-337.19
1200	28.11	29.91	18.75	16.54	-207.34	-90.79	-93.79	-1.63	119.43	75.98	-251.36	-333.31
1250	29.80	31.68	19.79	18.94	-205.13	-87.87	-91.15	1.44	121.16	78.67	-248.57	-329.41
1300	31.51	33.45	20.83	21.38	-202.90	-84.93	-88.49	4.55	122.91	81.39	-245.76	-325.49
1350	33.22	35.24	21.86	23.85	-200.64	-81.97	-85.80	7.71	124.66	84.12	-242.94	-321.55
1400	34.94	37.03	22.90	26.34	-198.35	-78.99	-83.09	10.92	126.42	86.87	-240.11	-317.60
1450	36.68	38.84	23.94	28.87	-196.03	-76.00	-80.37	14.16	128.18	89.63	-237.27	-313.63
1500	38.42	40.65	24.98	31.41	-193.69	-72.99	-77.62	17.45	129.96	92.40	-234.43	-309.65

$$= - 802.30 \text{ kJ/mol,}$$

which is equal to the so-called heat of combustion for methane gas.

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Example 2.9. Calculate the reaction enthalpy of the combustion reaction of propane gas

$$\underbrace{C_3H_8(g) + 5O_2(g)}_{A} \rightarrow \underbrace{3CO_2(g) + 4H_2O(g)}_{B} \tag{2.17}$$
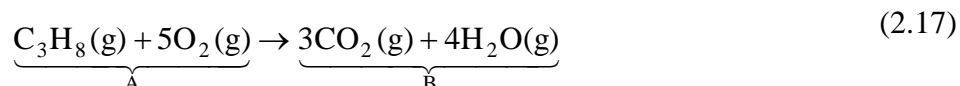
at a temperature of 450 K using the average specific heat capacity values at a temperature range of 298.15-400 K and compare the result with the value calculated using table 2.4. First, let's calculate the enthalpies of different compounds with enthalpies of formation and average specific heat capacities (table 2.3)

$$C_3H_8(g), \ h^o = \Delta H^\circ_f(T_O) + \overline{c}_p^{\,o} \ (T - T_O) = -105.8 + 93.2 \cdot 10^{-3} \cdot (450 - 298.15)$$

$$= -91.65 \text{ kJ/mol}$$

$$CO_2(g), \ h^o = -393.5 + 40.2 \cdot 10^{-3} \cdot (450 - 298.15) = -387.05 \text{ kJ/mol}$$

$$O_2(g), \ h^o = 0 + 30.0 \cdot 10^{-3} \cdot (450 - 298.15) = +4.55 \text{ kJ/mol}$$

$$H_2O(g), \ h^o = -241.8 + 34.2 \cdot 10^{-3} \cdot (450 - 298.15) = -236.61 \text{ kJ/mol}$$

$$\Delta H^o = H(B) - H(A) =$$
$$\left\{ 3h^o\left[CO_2(g)\right] + 4h^o\left[H_2O(g)\right] \right\} - \left\{ h^o\left[C_3H_8(g)\right] + 5h^o\left[O_2(g)\right] \right\}$$

$$\Delta H^o = \{3 \cdot (-387.05) + 4 \cdot (-236.61)\} - \{(-91.65) + 5 \cdot 4.55\} \text{ kJ/mol}$$

$$= -2012 \text{ kJ/mol.}$$

The same calculation using values in table 2.4

$$\Delta H^o = [3 \cdot (-387.42) + 4 \cdot (-236.64)] - [(-90.62) + 5 \cdot 4.56] =$$

$$-2041 \text{ kJ/mol.}$$

The result calculated with table 2.4 is naturally more accurate since its enthalpies have been calculated with consideration to the temperature dependence of specific heat capacity.

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Table 2.4 is excellent when calculating for example gas reactors. The enthalpies of gases entering and exiting the reactor at given temperatures can be found directly in table 2.4 and the power of heat absorbed or emitted by the reactor can be calculated with the difference in the enthalpy streams.

Example 2.10. Calculate the heat released in reaction (2.17) when propane gas and oxygen enter the reactor at a temperature of 350K and the products carbon dioxide and water vapor exit it at a temperature of 450K. From table 2.4 we get that

$$\Delta H^o = [3(- 387.42) + 4\cdot(- 236.64)] - [(- 100.90) + 5\cdot 1.53] = - 2015.57 \text{ kJ/mol}$$

which means that the power of heat released is 2016 kW when 1 mol/s of propane gas is combusted.

Example 2.11. Table 2.4 is also very convenient when analyzing for example flue gas losses. In an example presented later in chapter 12 the composition of flue gases for a certain light fuel oil has been calculated with an air factor of 1.15 per one kilogram of fuel:

O_2	15.6 mol/kg fuel
Ar	5.3 mol/kg fuel
N_2	451.3 mol/kg fuel
CO_2	71.5 mol/kg fuel
H_2O	67.8 mol/kg fuel

If the flue gases exit the boiler at a temperature of 450 K, how much additional power would be gained if the flue gases were cooled to 350 K, when the amount of oil combusted is 0.2 kg/s? Additional energy gained per one kilogram of oil combusted is

$$\Delta H^o = \sum_i n_i \left[h_i(450K) - h_i(350K) \right]$$
$$= 15.6(4.56 - 1.53) + 451.3(4.44 - 1.51)$$
$$+ 71.5[- 387.42 - (- 391.53)]$$
$$+ 67.8[- 236.64 - (- 240.08)]$$
$$+ 5.3(3.16 - 1.08)$$
$$= 1.908\cdot 10^3 \text{ kJ/kg fuel}$$

and therefore, the additional power is

$$\phi = 0.2 \text{ kg/s} \cdot 1.908\cdot 10^3 \text{ kJ/kg} = 382 \text{ kW}.$$

Example 2.12. Flue gas loss means the enthalpy stream along with flue gases compared to a situation where the flue gases would exit at the standard state temperature of 25 °C. In the previous example the flue gas losses when the flue gases exit at a temperature of 350 K can be calculated using table 2.4 with:

$$\Delta H^o = \sum_i n_i \left[h_i^o(350K) - h_i^o(298.15K) \right]$$

$= 15.6(1.53 - 0) + 451.3(1.51 - 0)$
$+ 71.5[(- 391.53) - (- 393.52)]$
$+ 67.8[(- 240.08) - (- 241.83)]$
$+ 5.3(1.08 - 0) = 972.0$ kJ/kg fuel.

The flue gas losses are $\phi = 0.2 \cdot 972.0 = 194.4$ kW. These examples are further discussed in chapter 4 and calculations based on tabulated enthalpies and heating values of fuels are also presented.

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2.4.2 Pressure dependence of enthalpy and specific heat capacity

Generally, the specific heat capacity of a compound is also dependent on pressure: $c_p = c_p(T,p)$. According to equation (2.8)

$$\frac{\partial h}{\partial p} = v - T \frac{\partial v}{\partial T}, \tag{2.18}$$

differentiating the definition of specific heat capacity

$$c_p = \frac{\partial h}{\partial T}$$

with respect to pressure and taking into account equation (2.18) results in

$$\frac{\partial c_p}{\partial p} = \frac{\partial}{\partial p}\left(\frac{\partial h}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial h}{\partial p}\right) = \frac{\partial}{\partial T}\left(v - T\frac{\partial v}{\partial T}\right) = \frac{\partial v}{\partial T} - \frac{\partial v}{\partial T} - T\frac{\partial^2 v}{\partial T^2}.$$

The pressure dependence of specific heat capacity is therefore

$$\frac{\partial c_p}{\partial p} = -T\frac{\partial^2 v}{\partial T^2} \tag{2.19}$$

where $v = v(T,p)$ is molar specific volume (m^3/mol).

Example 2.13. According to the ideal gas law

$$\frac{V}{N} = v(T,p) = RT/p, \tag{2.20}$$

where R = 8.314 J/(mol K). Therefore,

$$\frac{\partial^2 v}{\partial T^2} = 0$$

and for an ideal gas

$$c_p(T,p) = c_p(T). \tag{2.21}$$

For a real gas $\partial^2 v/\partial T^2 \neq 0$ and therefore c_p is also a function of pressure. A gas acts like an ideal gas the further the gas is from the critical point and therefore, the specific heat capacity is only dependent on temperature. In flue gas calculations, the gases can be considered as ideal gases.

Similarly, the specific volume of solids and liquids is often approximately linearly dependent on temperature T. Therefore, according to equation (2.19), c_p is only a function of temperature with high accuracy. An important exception is for example water and water vapor at high temperatures and pressures. At high pressures water vapor deviates significantly from an ideal gas. The deviation is greater the closer to the critical point the vapor is. This is also true in general for other liquids and gases near the critical point.

Example 2.14.

$$\text{Water vapor: } c_p \text{ (573.15 K, 1.0 bar)} = 2.010 \frac{\text{kJ}}{\text{kg K}} = 36.18 \frac{\text{J}}{\text{mol K}},$$

$$\text{water vapor: } c_p \text{ (573.15 K, 75 bar)} = 4.686 \frac{\text{kJ}}{\text{kg K}} = 84.35 \frac{\text{J}}{\text{mol K}},$$

$$\text{water: } c_p \text{ (573.15 K, 100 bar)} = 5.692 \frac{\text{kJ}}{\text{kg K}} = 102.46 \frac{\text{J}}{\text{mol K}},$$

$$\text{water: } c_p \text{ (573.15 K, 190 bar)} = 5.350 \frac{\text{kJ}}{\text{kg K}} = 96.30 \frac{\text{J}}{\text{mol K}}.$$

Example 2.15. For solid substances approximately

$$\gamma \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right) = 10^{-5}...2.0 \cdot 10^{-4} \, K^{-1},\tag{2.22}$$

and therefore, at room temperature $T = 298.15$ K the pressure dependence of enthalpy

$$\left(\frac{\partial h}{\partial p}\right)_T = v(1 - T\gamma) = (0.9970...0.9404)v.\tag{2.23}$$

Example 2.16. For an ideal gas

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\frac{R}{p} = 0,$$

which means that enthalpy is only dependent on temperature:

$$h(T,p) = h(T).\tag{2.24}$$

For non-ideal gases the specific enthalpy is a function of temperature and pressure. In addition, generally speaking the state and state functions of the components of a mixture are also dependent on the mole amounts of the components $n_1,\ldots,n_m$.

If the enthalpy of formation $\Delta H_f^o(T_o)$, specific heat capacity $c_p(T,p)$ and specific volume $v(T,p)$ at the standard state are known, the enthalpy of a compound can be calculated at any temperature T_1 and pressure p_1

$$h(T_1,p_1) = \Delta H_f^o(T_o) + \int_{T_0}^{T_1}\left(\frac{\partial h}{\partial T}\right)_{p=p^o} dT + \int_{p^o}^{p_1}\left(\frac{\partial h}{\partial p}\right)_{T=T_1} dp\tag{2.25}$$

i.e. with the definition $c_p = \dfrac{\partial h}{\partial T}$ and equation (2.18)

$$h(T_1,p_1) = \Delta H_f^o(T_o) + \int_{T_0}^{T_1} c_p(T,p_o)dT + \int_{p_0}^{p_1}\left[v(T_1,p) - T_1\left(\frac{\partial v}{\partial T}\right)_{T=T_1}\right]dp\tag{2.26}$$

2.5 Enthalpy at the absolute zero

When the enthalpy value is defined with equation (2.13) at a temperature of T_o, the enthalpy of a compound or an element at the absolute zero can be calculated with equation (2.16). This enthalpy is noted as $h°(0)$ [$H°(0)$ in tables]. By taking into consideration the definition (2.13), i.e. $h°(T_o) \equiv \Delta H_f°(T_o)$, according to equation (2.16) we get

$$h°(0) - h°(T_o) = \int_{T_0}^{T_{tr}} c_p \, dT + \Delta H°_{tr}(T_{tr}) + \int_{T_{tr}}^{0} c_p \, dT. \tag{2.27}$$

If a gas is analyzed, another phase change term, the crystallization of liquid and the enthalpy change associated with it, has to be added to equation (2.27). If a solid substance is analyzed, phase change terms are not necessarily present. However, a phase change in solid substances is possible between different crystal structures.

Values of $[h°(0) - h°(T_o)]$ are already calculated for different compounds in table books of chemical thermodynamics, as well as values of $[h°(T) - h°(T_o)]$ at certain temperature increments. For example, a table of values for aluminum oxide is presented below.

_____

Example 2.17. Aluminum is produced from aluminum oxide (Al_2O_3) by heating it up to its melting point and performing an electrolysis. Calculate the amount of energy required to heat up aluminum oxide from 500 K to a temperature of 2500 K. Liquification occurs at a temperature of 2327 K, which has an endothermic heat of melting of 111.086 kJ/mol. From table 2.5 we can directly read ($T_o = T_r = 298.15$ K)

$h°(T = 500 \text{ K}) - h° (T_o) = 19.145$ kJ/mol (crystal, alpha (corundum))

$h°(T = 2500 \text{ K}) - h°(T_o) = 399.143$ kJ/mol, (liquid)

and therefore, the required amount of energy is

$h°(T = 2500 \text{ K}) - h°(500 \text{ K}) = 399.143 - 19.145 = 379.998$ kJ/mol.

As seen from the table below, this amount of energy also includes the amount of heat required by the liquification of aluminum oxide, i.e. the heat of melting at a temperature of 2327K.
_____

Table 2.5. Thermodynamic properties of aluminum oxide Al$_2$O$_3$(cr, l) [1].

Aluminum Oxide (Al$_2$O$_3$)   Al$_2$O$_3$(cr,l)

Enthalpy Reference Temperature = T$_r$ = 298.15 K				Standard State Pressure = p° = 0.1 MPa		
	— J K^{-1}mol^{-1} —			— kJ mol^{-1} —		
T/K	C$_p^o$	S°	-[G°-H°(T$_r$)]/T	H°-H°(T$_r$)	Δ$_f$H°	Δ$_f$G°	Log K$_f$
0	0.	0.	INFINITE	-10.020	-1663.608	-1663.608	INFINITE
100	12.855	4.295	101.230	-9.693	-1668.606	-1641.642	857.506
200	51.120	24.880	57.381	-6.500	-1673.383	-1612.656	421.183
298.15	79.015	50.950	50.950	0.	-1675.692	-1582.275	277.208
300	79.416	51.440	50.951	0.147	-1675.717	-1581.696	275.398
400	96.086	76.779	54.293	8.995	-1676.342	-1550.226	202.439
500	106.131	99.388	61.098	19.145	-1676.045	-1518.718	158.659
600	112.545	119.345	69.177	30.101	-1675.300	-1487.319	129.483
700	116.926	137.041	77.632	41.586	-1674.391	-1456.059	108.652
800	120.135	152.873	86.065	53.447	-1673.498	-1424.931	93.038
900	122.662	167.174	94.296	65.591	-1672.744	-1393.908	80.900
1000	124.771	180.210	102.245	77.965	-1693.394	-1361.437	71.114
1100	126.608	192.189	109.884	90.535	-1692.437	-1328.286	63.075
1200	128.252	203.277	117.211	103.280	-1691.366	-1295.228	56.380
1300	129.737	213.602	124.233	116.180	-1690.190	-1262.264	50.718
1400	131.081	223.267	130.965	129.222	-1688.918	-1229.393	45.869
1500	132.290	232.353	137.425	142.392	-1687.561	-1196.617	41.670
1600	133.361	240.925	143.628	155.675	-1686.128	-1163.934	37.999
1700	134.306	249.039	149.592	169.060	-1684.632	-1131.342	34.762
1800	135.143	256.740	155.333	182.533	-1683.082	-1098.841	31.888
1900	135.896	264.067	160.864	196.085	-1681.489	-1066.426	29.318
2000	136.608	271.056	166.201	209.710	-1679.858	-1034.096	27.008
2100	137.319	277.738	171.354	223.407	-1678.190	-1001.849	24.920
2200	138.030	284.143	176.336	237.174	-1676.485	-969.681	23.023
2300	138.741	290.294	181.158	251.013	-1674.743	-937.593	21.293
2327.000	138.934	291.914	182.434	254.761	ALPHA <--> LIQUID		
2327.000	192.464	339.652	182.434	365.847	TRANSITION		
2400	192.464	345.597	187.307	379.896	-1557.989	-909.127	19.787
2500	192.464	353.454	193.796	399.143	-1550.905	-882.237	18.433
2600	192.464	361.002	200.083	418.389	-1543.853	-855.629	17.190
2700	192.464	368.266	206.179	437.636	-1536.832	-829.292	16.044
2800	192.464	375.265	212.093	456.882	-2117.645	-801.279	14.948
2900	192.464	382.019	217.837	476.128	-2108.494	-754.429	13.589
3000	192.464	388.544	223.419	495.375	-2099.372	-707.892	12.325
3100	192.464	394.855	228.848	514.621	-2090.279	-661.658	11.149
3200	192.464	400.965	234.132	533.868	-2081.214	-615.719	10.051
3300	192.464	406.888	239.277	553.114	-2072.175	-570.063	9.023
3400	192.464	412.633	244.292	572.360	-2063.162	-524.679	8.061
3500	192.464	418.212	249.182	591.607	-2054.176	-479.561	7.157
3600	192.464	423.634	253.953	610.853	-2045.213	-434.699	6.307
3700	192.464	428.908	258.610	630.100	-2036.276	-390.086	5.507
3800	192.464	434.040	263.160	649.346	-2027.363	-345.712	4.752
3900	192.464	439.040	267.606	668.592	-2018.474	-301.574	4.039
4000	192.464	443.912	271.953	687.839	-2009.609	-257.664	3.365

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

$$\Delta H = \int_{298.15}^{350} c_p dT = 38.27 \cdot (350 - 298.15) = 1.984 \text{kJ/mol}$$