Chapter 5
Influence of Temperature and Pressure on Transformations

The chemical potential can be regarded as constant only in a first approximation. Frequently, temperature and pressure have a decisive influence on the chemical potential and therefore on the course of chemical processes. Water freezes in the cold and evaporates in the heat. Ice melts under the blades of ice skates and butane gas (the fuel of a cigarette lighter) becomes liquid when compressed. Therefore, a more detailed approach has to consider the temperature and pressure dependence of μ. Often linear approaches to these dependencies suffice. If the corresponding temperature and pressure coefficients are given, it is easily possible to predict the behavior of the substances when they are heated, compressed, etc. The melting, sublimation points, etc., can be calculated, but also the minimum temperature needed for a particular reaction. Only the pressure coefficient of gases shows a strong pressure dependence itself; therefore, the linear approach is only valid in a small pressure range. For wider application, a logarithmic approach has to be used.

5.1 Introduction

Until now, the tabular values we have used were the so-called standard values based upon room temperature and standard pressure (298 K and 100 kPa). For dissolved substances, the standard concentration is 1 kmol m^{-3}. Up to this point, our statements about the possibility of a transformation have been valid for these conditions only.

However, temperature and pressure often have a decisive influence on the chemical potential and therefore on the course of chemical processes. Water freezes in the cold and evaporates in the heat. Cooking fat melts in a frying pan and pudding gels while cooling, ice melts under the blades of ice skates, and butane gas becomes liquid when compressed. The chemical potential μ is not a material constant, but depends upon temperature, pressure, and a number of other parameters.

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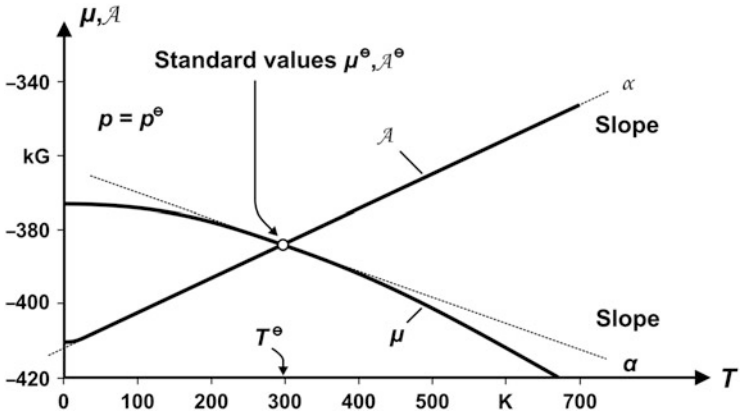


Fig. 5.1 Chemical potential of table salt and chemical drive to decompose according to $NaCl \rightarrow Na + \frac{1}{2}\ Cl_2$ depending upon temperature (at constant pressure $p^{\ominus}$).

5.2 Temperature Dependence of Chemical Potential and Drive

Introduction To begin, let us consider as a typical example the change with temperature in the chemical potential of table salt μ(NaCl) (Fig. 5.1). For comparison, the graphic also shows the temperature dependence of the chemical drive of table salt to decompose into the elements $\mathcal{A}(NaCl \rightarrow Na + \frac{1}{2}Cl_2)$.

It is striking that the chemical potential *falls* more and more steeply with *increasing temperature*. Except for a very few exceptions of dissolved substances (e.g., $Ca^{2+}|w$), all substances exhibit this behavior. The tendency of a substance to transform generally decreases when it is put into a warmer environment.

The chemical drive $\mathcal{A}(T)$, which is calculated from the temperature-dependent potentials, exhibits a noticeably more linear gradient than the $\mu(T)$ curves. Both curves intersect at the standard temperature $T^{\ominus}$ because the chemical potential of a substance at standard conditions corresponds to the drive to decompose into the elements (here sodium and chlorine).

The drop of potential appears, at first glance, to contradict the observation that reactions progress more readily and more quickly at higher temperatures than at lower ones. But it should be noted that a higher rate of reaction does not necessarily mean a stronger chemical drive. This can also be caused by a smaller or even vanishing inhibition as is actually often the case in chemical reactions. The strong decrease of inhibition resulting from an increase of warming masks the mostly weak change to the drive $\mathcal{A}$. Moreover, it should be remembered that $\mathcal{A}$ is determined by the difference of the chemical potentials of the starting substances and the final products, and *not* by the absolute levels of potentials. Since the potentials of the starting substances as well as of the final products decrease as a result of an increase in temperature, the potential difference which is alone

responsible for the reaction drive does not necessarily decrease. It can remain constant or even increase, as in our example.

Temperature Coefficient In order to describe the drop of potential with increasing temperature, we will be content with a simple approach at first. For example, if one wishes to show how the length l of a rod changes with temperature, this can be done with the help of a *temperature coefficient* which tells us by how much the length increases when its temperature is changed by 1 K. The increase in length for a temperature increase from an initial value of T_0 to a value of T can be described by a *linear* equation as long as $\Delta T = T - T_0$ is not too large:

$$l = l_0 + \varepsilon \cdot (T - T_0). \tag{5.1}$$

The initial value of the length is represented by l_0 and ε represents the temperature coefficient.

To indicate the change of chemical potential as a result of warming, we proceed exactly in the same manner:

$$\mu = \mu_0 + \alpha \cdot (T - T_0). \tag{5.2}$$

Here, μ_0 characterizes the initial value of the chemical potential. This represents a value at arbitrarily chosen values of temperature T_0, pressure p_0, and concentration c_0 (in contrast to the standard value $\mu^{\ominus}$). However, standard values often serve as the initial values of a calculation, so that in special cases, $\mu_0 = \mu^{\ominus}$, but this is not necessarily the case. The *temperature coefficient* α represents the slope of the function $\mu(T)$ at the point $(T_0; \mu_0)$ (it is therefore strictly valid only for the reference temperature T_0), and is therefore almost always *negative*, as we have seen.

For the temperature dependence of the chemical drive $\mathcal{A}$ of a transformation

$$\mathrm{B} + \mathrm{B}' + \ldots \rightarrow \mathrm{D} + \mathrm{D}' + \ldots$$

we obtain analogously:

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T - T_0). \tag{5.3}$$

The temperature coefficient α of the drive can be calculated by the same easy to remember procedure as the drive itself:

$$\alpha = \alpha(\mathrm{B}) + \alpha(\mathrm{B}') + \ldots - \alpha(\mathrm{D}) - \alpha(\mathrm{D}') - \ldots \tag{5.4}$$
$$(\text{Remember}: \mathcal{A} = \mu(\mathrm{B}) + \mu(\mathrm{B}') + \ldots - \mu(\mathrm{D}) - \mu(\mathrm{D}') - \ldots).$$

If we take room conditions as the starting point, the error is about 1 kG for low-molecular substances for ΔT values of about ± 100 K. This approximation remains useful for rough estimates up to $\Delta T \approx 1{,}000$ K and above, although $\mu(T)$ falls

sharply with rising temperature. This remarkable and (for applications) important circumstance is based upon the fact that it is not the potentials that are decisive in chemical processes, but the drives. When taking the difference $\mathcal{A} = \sum \mu_{\text{reactants}} - \sum \mu_{\text{products}}$, the progressive contributions of the functions $\mu(T)$ largely cancel.

If higher precision is desired, the approach can be easily improved by adding more terms to the equation:

$$\mu = \mu_0 + \alpha \cdot \Delta T + \alpha' \cdot (\Delta T)^2 + \alpha'' \cdot (\Delta T)^3 + \ldots . \tag{5.5}$$

Of course, there are other possible approaches; reciprocals for instance, or logarithmic terms. However, we do not wish to go into mathematical refinements of this type here because it is astounding how far one can actually go with the linear approximation. It is our goal here to show this.

Table 5.1 shows the chemical potential $\mu^{\ominus}$ as well as its temperature coefficient α for some substances. Along with the already mentioned basic rule which states that the temperature coefficient α is (almost) always negative, another rule (which almost all substances follow) becomes apparent when the α values are compared for changes of state of aggregation. The temperature coefficient α of the chemical potential of a substance B becomes increasingly negative when the phase changes from the solid to the liquid and finally to the gaseous state. The jump corresponding to the second transition (represented by the sign $\ll$) is considerably greater than the one corresponding to the first one. For a substance in an aqueous solution, α is mostly similar to that of the liquid state. The values scatter more strongly, though, so that we cannot easily fit α(B|w) into the other α values:

Table 5.1 Chemical potential μ and its temperature coefficient α for some selected substances at standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m^{-3}).

Substance	Formula	$\mu^{\ominus}$ (kG)	α (G K^{-1})
Iron	Fe|s	0	−27.3
	Fe|l	5.3	−35.6
	Fe|g	368.3	−180.5
Graphite	C|graphite	0	−5.7
Diamond	C|diamond	2.9	−2.4
Iodine	I_2|s	0	−116.1
	I_2|l	3.3	−150.4
	I_2|g	19.3	−260.7
	I_2|w	16.4	−137.2
Water	H_2O|s	−236.6	−44.8
	H_2O|l	−237.1	−70.0
	H_2O|g	−228.6	−188.8
Ammonia	NH_3|l	−10.2	−103.9
	NH_3|g	−16.5	−192.5
	NH_3|w	−26.6	−111.3
Calcium(II)	Ca^{2+}|w	−553.6	+53.1

$$\alpha(\mathrm{B}|\mathrm{g}) << \alpha(\mathrm{B}|\mathrm{l}) < \alpha(\mathrm{B}|\mathrm{s}) < 0.$$
$$\longleftarrow \alpha(\mathrm{B}|\mathrm{w}) \longrightarrow$$

For clarification, we will single out the values for iodine at standard conditions given in G K^{-1} from Table 5.1:

$$-260.7 << -150.4 < -116.1 < 0.$$
$$-137.2$$

(As we will see in Sect. 9.3, the temperature coefficient α corresponds to the negative molar entropy S_m, i.e., $\alpha = -S_m$. Anticipating this can help us to remember the two rules above more easily: First, in Chap. 3, we demonstrated that the molar entropy is always positive; the negative sign of the temperature coefficient easily results from this (the rare exceptions mentioned above will be discussed in detail in Sect. 8.4). Second, the fact that the molar entropy of a liquid is greater than that of a solid, and the molar entropy of a gas is much greater than that of a liquid (see Sect. 3.9), leads to the sequence above.)

Phase Transition The chemical potential of gases therefore decreases especially fast with increase in temperature. Their tendency to transform decreases most strongly so that, by comparison to other states, the gaseous state becomes more and more stable. This simply means that, as a result of temperature increase, all other states must eventually transform into the gaseous state. At high temperatures, gases possess the weakest tendency to transform and therefore represent the most stable form of matter.

We will use water to take a closer look at this behavior. Under standard conditions, the chemical potential of ice, water, and water vapor has the following values:

	$H_2O\|s$	$H_2O\|l$	$H_2O\|g$
$\mu^{\ominus}$(kG)	−236.6	−237.1	−228.6

One sees here that under these conditions, ice melts, and water vapor condenses because water in its liquid state has the lowest chemical potential and therefore the weakest tendency to transform. However, this changes if the temperature is raised or lowered sufficiently. For easy calculation, we will consider a temperature change of ±100 K. The following results are obtained using the linear approach:

	$H_2O\|s$	$H_2O\|l$	$H_2O\|g$
α(G K^{-1})	−45	−70	−189
μ(398 K)(kG)	−241	−244	−248
μ(198 K)(kG)	−232	−230	−210

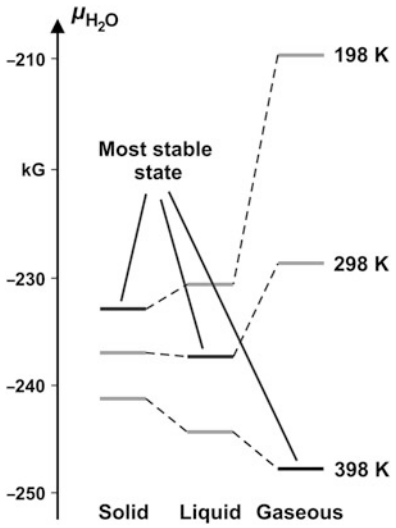


Fig. 5.2 Chemical potential of water in various states at 198, 298, and 398 K.

We see that at 398 K (125 °C), the chemical potential of water vapor has the smallest value and that water vapor must result from the other forms, while at 198 K (−75 °C), ice must develop. This result is represented graphically in Fig. 5.2.

Phase Transition Temperatures How to calculate the *phase transition temperatures* now appears obvious: If a substance like lead is solid at room temperature, this is because its chemical potential has its lowest value in the solid state. The potential of liquid lead has to exceed that of solid lead; otherwise, at room temperature, it would be liquid like mercury. We will now visualize this in a diagram (Fig. 5.3).

μ(Pb|s) as potential of an element at room temperature (and standard pressure) is equal to zero since this value has been arbitrarily chosen as the zero point of the μ scale. Under these conditions, μ(Pb|l) must lie above this. The chemical potentials decrease with warming. This happens more quickly in the liquid state than in the solid (according to the sequence presented above: $\alpha(B|l) < \alpha(B|s) < 0$). For this reason, the curves must intersect at some point, say at the temperature T_{sl}. This T_{sl} is the *melting temperature* (melting point) of lead because below T_{sl}, the most stable state of lead is the solid state; above T_{sl}, however, the most stable state is the liquid state. In order to indicate the phase transition in question, the symbols for the corresponding states of aggregation are inserted as indices (see also the comment in Sect. 3.9).

We can calculate the temperature T_{sl}. In order to do this we have to consider the melting process

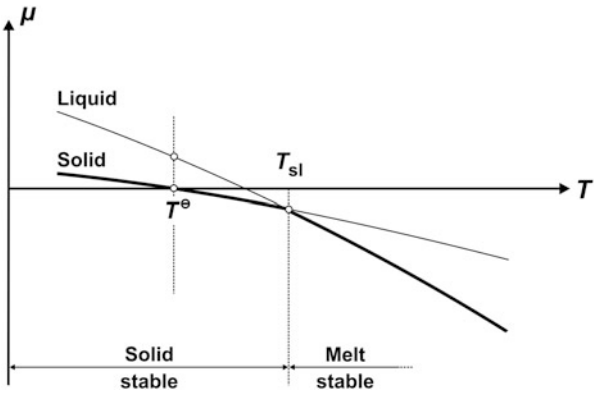


Fig. 5.3 Temperature dependence of the chemical potential of the solid and liquid phase of a substance (The lowest chemical potential for each is highlighted.).

$$\mathrm{Pb}|\mathrm{s} \rightarrow \mathrm{Pb}|\mathrm{l}.$$

T_{sl} is the temperature at which the chemical potentials of solid and liquid phase are just equal,

$$\mu_s = \mu_l. \tag{5.6}$$

At this temperature, the two phases are in equilibrium. The temperature dependence of μ is expressed by the linear approximation:

$$\mu_{s,0} + \alpha_s \cdot (T_{sl} - T_0) = \mu_{l,0} + \alpha_l \cdot (T_{sl} - T_0).$$

By transforming this, we obtain

$$\mu_{s,0} - \mu_{l,0} = -(\alpha_s - \alpha_l) \cdot (T_{sl} - T_0)$$

and finally

$$T_{sl} = T_0 - \frac{\mu_{s,0} - \mu_{l,0}}{\alpha_s - \alpha_l} = T_0 - \frac{\mathcal{A}_0}{\alpha}. \tag{5.7}$$

The derivation is somewhat shortened when the equivalent of Eq. (5.6), $\mathcal{A} = \mu_s - \mu_l = 0$, is used as a starting point for the existence of a state of equilibrium. If the temperature dependence of the chemical drive is taken into account [Eq. (5.3)], we have

$$\mathcal{A}_0 + \alpha \cdot (T_{sl} - T_0) = 0$$

and therefore in the end as above

$$T_{\mathrm{sl}} = T_0 - \frac{\mathcal{A}_0}{\alpha}.$$

Of course, strictly speaking, this mathematical relationship is not completely accurate because our formula for temperature dependence is only an approximation. The smaller ΔT ($:=T_{\mathrm{sl}} - T_0$) is, the more exact the calculated value will be. The melting point of lead is actually 601 K. Based on the tabulated standard values (Sect. A.2.1 in the Appendix), our calculation yields

$$T_{\mathrm{sl}} = 298\,\mathrm{K} - \frac{0 - 2220}{(-64.8) - (-71.7)} \frac{\mathrm{G}}{\mathrm{G\,K^{-1}}} = 620\,\mathrm{K}.$$

The result is surprisingly good for the rather rough approximation.

We will now complete the $\mu(T)$ diagram above by adding the chemical potential of lead vapor (Fig. 5.4). At room temperature, the chemical potential of vapor lies much higher than that of the liquid phase. However, with rising temperature, $\mu(\mathrm{Pb|g})$ falls rather steeply, as is usual in all gases. At some temperature T_{lg} the potential of lead vapor intersects with that of liquid lead. When this temperature is exceeded, the melted lead undergoes a transition to vapor because now vapor is the most stable state. T_{lg} is nothing other than the *boiling temperature* (boiling point) of lead melt. The boiling temperature can be calculated in the same manner as the melting temperature, only now the potentials and their temperature coefficients for liquid and gaseous states will be used.

There are substances for which the chemical potential of the vapor is relatively low compared to that of the melt. The potential of the vapor can then intersect that of the solid below the melting point. This means that there is no temperature (for a given pressure) at which the liquid phase exhibits the lowest chemical potential and

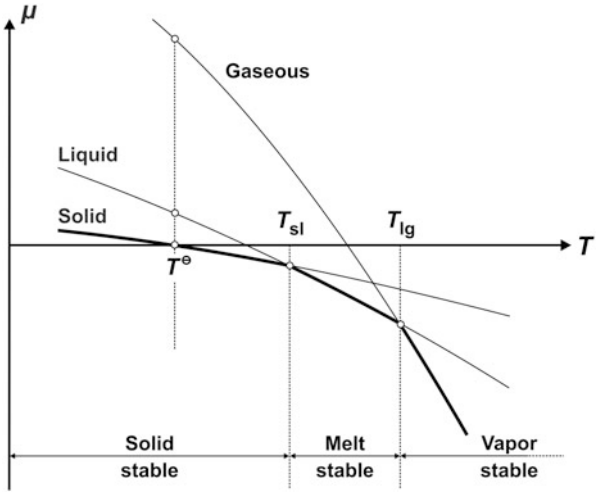


Fig. 5.4 Temperature dependence of the chemical potentials of a substance as solid, melt, or vapor.

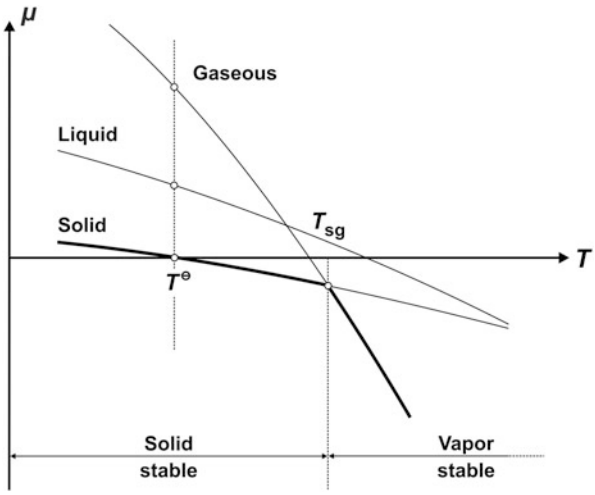


Fig. 5.5 Chemical potentials of all phases as a function of temperature in the case of sublimation.

is therefore stable. Such substances do not melt when warmed but transform immediately into the vapor state (Fig. 5.5). This phenomenon is called *sublimation*.

An excellent example of such a substance is frozen carbon dioxide which has the characteristic of vaporizing without melting. Because of this it is also called "dry ice." *Sublimation temperatures* (sublimation points) T_{sg} can be calculated based on the same procedure as used for melting and boiling temperatures, respectively.

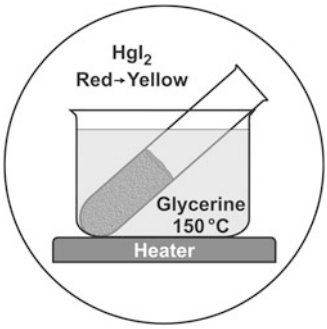
Other transitions can be dealt with in the same way. A good object for demonstration is the already mentioned mercury iodide (cf. Sect. 4.6):

	HgI_2|yellow	HgI_2|red
$\mu^{\ominus}$(kG)	−101.1	−101.7
$\alpha(GK^{-1})$	−186	−180

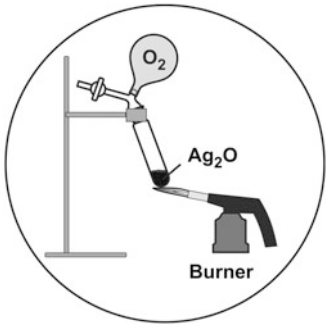
When heated, the temperature coefficient of the yellow form decreases more quickly than that of the red one because $\alpha(HgI_2|\text{yellow}) < \alpha(HgI_2|\text{red}) < 0$, so that above a certain temperature, $\mu(HgI_2|\text{yellow})$ falls below $\mu(HgI_2|\text{red})$, making the yellow form the more stable modification. The transition temperature (about 398 K or 125 °C) can be calculated just like the melting temperature of lead and can be easily verified by experiment (Experiment 5.1). The property of some substances to change color due to a change in temperature is called *thermochromism*.

Reaction Temperatures Chemists are mostly interested in "real" chemical reactions. Because the temperature changes in gases have the strongest effect on their potentials, they are what shapes the behavior of reactions. Processes which produce more gas than is used up (so-called *gas forming* reactions) benefit from the strongly negative temperature coefficients α of gases when the temperature rises. In contrast, the chemical drive of a *gas binding* reaction is weakened by a rise in temperature. Consider the example of thermal decomposition of silver oxide:

Experiment 5.1 *Thermochromism of HgI_2*: A test tube containing red-orange mercury(II) iodide is slowly heated in a glycerine bath. At 398 K the iodide undergoes phase transition from the red-orange to the pale yellow modification.



Experiment 5.2 *Heating of silver oxide*: When the blackish brown silver oxide is heated by a burner, the generation of a gas is detectable by the slow blowing up of the balloon. Subsequently, the gas can be identified as oxygen with a glowing splint. White shiny silver metal remains in the test tube.



	$2\,Ag_2O\|s$	$\rightarrow 4\,Ag\|s$	$+\ O_2\|g$	
$\mu^{\ominus}$(kG):	$2\times(-11.3)$	4×0	0	$\Rightarrow \mathcal{A}^{\ominus} = -22.6$ kG
α (G K^{-1}):	$2\times(-121)$	$4\times(-43)$	-205	$\Rightarrow \alpha = +135$ G K^{-1}

The decomposition does not take place at room temperature due to the negative drive. However, since a gas should be formed, we expect that this process begins at a high enough temperature (Experiment 5.2). The minimum temperature T_D for the decomposition of Ag_2O is obtained from the condition that the combined chemical potentials of the initial and final substances must be equal or alternatively the chemical drive $\mathcal{A} = 0$:

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T_D - T_0) = 0.$$

In analogy to Eq. (5.7), we obtain for the decomposition temperature

$$T_D = T_0 - \frac{\mathcal{A}_0}{\alpha}.$$

Based on the initial values $T_0 = T^{\ominus}(= 298\,\text{K})$ and $\mathcal{A}_0 = \mathcal{A}^{\ominus}$, we obtain by inserting the $\mathcal{A}^{\ominus}$ and α values calculated above a decomposition temperature $T_D \approx 465$ K (i.e., 192 °C).

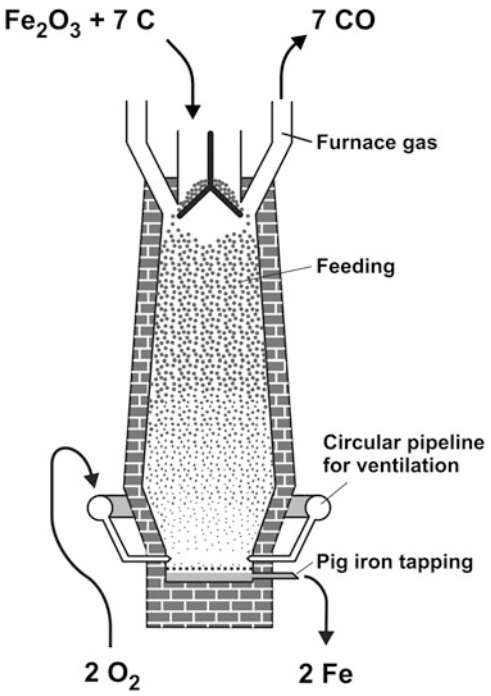


Fig. 5.6 Schematic of a blast furnace.

The same procedure can be used, for example, to calculate how strongly a compound containing crystal water must be heated in a drying oven in order to dehydrate it. Industrially important processes such as smelting of iron ore in a blast furnace (Fig. 5.6) can also be captured descriptively.

If the technical details are left out, a blast furnace can be considered a chemical reactor where iron ore, coal, and oxygen are introduced and furnace gas and pig iron exit. If this process uses the minimum amount of coal (in the conversion formula simplistically represented by carbon C|s (≈ graphite) it cannot take place at room temperature due to its negative chemical drive.

	Fe_2O_3|s + 3 C|s	→ 2 Fe|s + 3 CO|g		
$\mu^{\ominus}$(kG):	−741.0	3×0	2×0	3×(−137.2)	$\Rightarrow \mathcal{A}^{\ominus} = -329.4$ kG
α (G K^{-1}):	−87	3×(−6)	2×(−27)	3×(−198)	$\Rightarrow \alpha = +543$ G K^{-1}

However, a gas is formed, so we expect that the reaction should be possible at higher temperatures. If one wishes to find out if the 700 K in the upper part of the shaft of the furnace is hot enough, the drive must be approximated for this temperature according to $\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T - T_0)$ [Eq. (5.3)]. With a value of −111 kG, the drive is noticeably less negative, i.e., the potential difference between the reactants and products has become smaller, but the reaction still cannot take place. Again, the minimum temperature T_R needed for the reaction can be

approximated by an equation which appears very familiar to us [entirely equivalent to Eq. (5.7)]:

$$T_R = T_0 - \frac{\mathcal{A}_0}{\alpha}.$$

We therefore obtain a value for T_R of ≈ 900 K. Extra coal is needed for the furnace to reach this temperature. The chemical drive of the whole blast furnace process, beginning and ending with all substances at room temperature, is strongly positive because of the additional consumption of carbon:

$$\begin{array}{lcccccl} & \mathrm{Fe_2O_3|s} + & 7\ \mathrm{C|s} + & 2\ \mathrm{O_2|g} & \rightarrow 2\ \mathrm{Fe|s} + & 7\ \mathrm{CO|g} & \\ \mu^{\ominus}(\mathrm{kG}): & -741.0 \quad 7\times 0 & & 2\times 0 & & 7\times(-137.2) & \Rightarrow \mathcal{A}^{\ominus} = +219.4\ \mathrm{kG} \end{array}$$

Of course, all of these calculations depend upon access to the necessary data.

5.3 Pressure Dependence of Chemical Potential and Drive

Pressure Coefficient As previously stated, the value of the chemical potential of a substance depends not only upon temperature but upon pressure as well. Moreover, the potential generally *increases* when the *pressure increases* (Fig. 5.7).

In a small range of pressures, all the curves can be approximated as linear, comparable to the way in which we described the influence of temperature:

$$\mu = \mu_0 + \beta \cdot (p - p_0). \tag{5.8}$$

μ_0 is the starting value of the chemical potential for the initial pressure p_0. The pressure coefficient β is almost always *positive*.

Analogously, the pressure dependence of the chemical drive $\mathcal{A}$ of a transformation

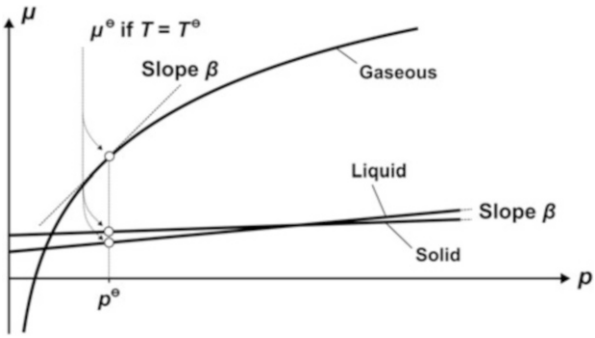


Fig. 5.7 Pressure dependence of the chemical potentials of a substance in solid, liquid, or gaseous state.

$$\mathrm{B} + \mathrm{B}' + \ldots \rightarrow \mathrm{D} + \mathrm{D}' + \ldots$$

results in

$$\mathcal{A} = \mathcal{A}_0 + \beta \cdot (p - p_0), \tag{5.9}$$

where the pressure coefficient β is:

$$\beta = \beta(\mathrm{B}) + \beta(\mathrm{B}') + \ldots - \beta(\mathrm{D}) - \beta(\mathrm{D}') - \ldots. \tag{5.10}$$

The linear approximation is useful for solid, liquid, as well as dissolved substances and for the drives of the corresponding transformations up to $\Delta p \approx 10^5$ kPa (= 1,000 bar). For obtaining general approximations, it is useful even up to 10^6 kPa (= 10,000 bar). In the case of gases and the drives of transformations in which gases participate, $\Delta p / p < 10\,\%$ is considered acceptable because the slope β of the corresponding curve changes relatively strongly with pressure. For greater ranges of pressure Δp, another approach must be applied to which we will be introduced later on (Sects. 5.5 and 6.5).

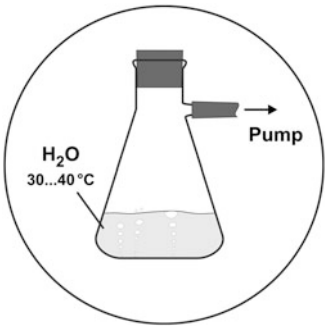
Table 5.2 shows the β values for the substances of Table 5.1. A rule similar to the one for temperature coefficients α is valid for pressure coefficients β. It is very useful for qualitative considerations:

$$0 < \beta(\mathrm{B|s} < \beta(\mathrm{B|l}) <<<< \beta(\mathrm{B|g})\ .$$
$$\longleftarrow \quad \beta(\mathrm{B|w}) \longrightarrow$$

Table 5.2 Chemical potential μ and its pressure coefficient β for some selected substances at standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m^{-3}).

Substance	Formula	$\mu^{\ominus}$ (kG)	β (μG Pa^{-1})
Iron	Fe|s	0	7.1
	Fe|g	368.3	24.8×10^3
Graphite	C|graphite	0	5.5
Diamond	C|diamond	2.9	3.4
Nitrogen	N_2|g	0	24.8×10^3
Iodine	I_2|s	0	51.5
	I_2|l	3.3	60.3
	I_2|g	19.3	24.8×10^3
	I_2|w	16.4	≈50
Water	H_2O|s	−236.6	19.8
	H_2O|l	−237.1	18.1
	H_2O|g	−228.6	24.8×10^3
Ammonia	NH_3|l	−10.2	28.3
	NH_3|g	−16.5	24.8×10^3
	NH_3|w	−26.6	24.1
Calcium(II)	Ca^{2+}|w	−553.6	−17.7

Experiment 5.3 *Boiling of lukewarm water at low pressure*: A suction flask is filled to one-third with lukewarm water, closed, and subsequently evacuated with a water aspirator. The water begins to boil.



To make this clear, we will again single out the values for iodine at standard conditions, this time given in μG Pa^{-1}:

$$0 < 51.5 < 60.3 <<<< 24.8\times10^3$$
$$\approx 50$$

Like any rule, this one has exceptions. For instance, β for some ions in an aqueous solution is negative and sometimes—as in the case of water—β in the solid state is greater than in the liquid state. This is exactly the opposite from what the rule would lead us to expect.

(In this case, as well, there is a relation to a molar quantity, namely the molar volume V_m: We have $\beta = V_m$ (compare Sect. 9.3). Because all molar volumes are basically positive, the pressure coefficient always has a positive sign. (The very few exceptions and their cause will be discussed in detail in Sect. 8.2.) The molar volume of a gas is far greater (by a factor of 1,000) than that of the condensed phases (liquid and solid). On the other hand, the molar volume of a liquid phase is usually greater than that of the solid phase so that the sequence above results.)

Phase Transition Raising the pressure generally causes the chemical potential to increase although, as already stated, the increase varies for the different states of aggregation. In the solid state, it is smallest and in the gaseous state, greatest. As a rule, the higher the pressure is, the more stable the solid state is compared to the others and the greater the tendency of the substance to undergo a transition to the crystalline state. Conversely, a pressure reduction results in a preference for the gaseous state.

Let us once more consider the behavior of water from this new viewpoint. The following table summarizes the necessary chemical potentials and pressure coefficients:

	$H_2O\|s$	$H_2O\|l$	$H_2O\|g$
$\mu^{\ominus}$(kG)	−236.6	−237.1	−228.6
$\beta(10^{-6}\,GPa^{-1})$	19.8	18.1	24.8×10^3

One sees that lukewarm water can boil at low pressure (Experiment 5.3), although, at room conditions, $\mu(H_2O|l) < \mu(H_2O|g)$, meaning liquid water is the

Experiment 5.4 *Causing warm water to boil by cooling*: Ice water is poured over a round-bottomed flask only filled with warm water and water vapor. The water begins to boil also in this case.

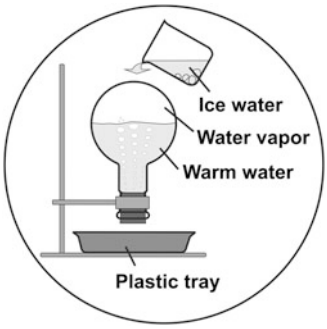
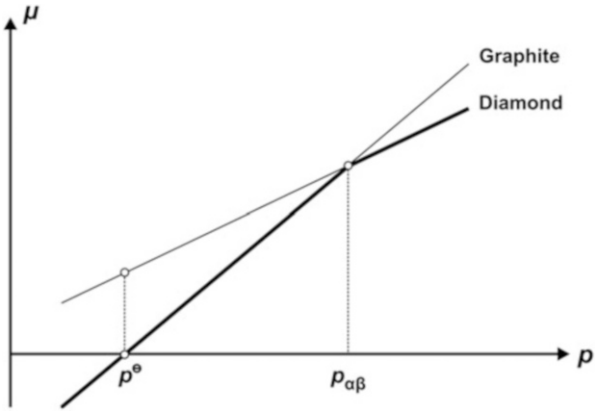


Fig. 5.8 Pressure dependence of the chemical potentials of graphite and diamond (the lowest chemical potential for each is again highlighted).



stable phase. But if the pressure is lowered enough by pumping the air above the water out of a closed container, $\mu(H_2O|g)$ will at some point fall below $\mu(H_2O|l)$, because β is especially great for the gaseous state. The reduction of pressure becomes noticeable by a strong decrease of chemical potential and the water begins to transform into water vapor by boiling.

But low pressure can also be created by cooling down water vapor which is in equilibrium with liquid water in a closed flask (Experiment 5.4). In the process, a part of the vapor condenses, leading to a decrease in pressure.

Phase Transition Pressure We shall take a closer look at a further example of the transition of a substance under pressure. Diamond is a high-pressure modification of carbon which should never appear at normal pressure. The most stable modification of carbon, the one with the lowest chemical potential, is graphite which we know from pencils. A characteristic of graphite is that its chemical potential increases more strongly with pressure than the potential of diamond so that, at one point, μ(C|graphite) should exceed μ(C|diamond) making it possible for diamond to form (Fig. 5.8).

At normal pressure and room temperature, μ(C|graphite) equals zero because this value has been arbitrarily set as the zero point of the μ scale. The $\mu(p)$ curve is

steeper for graphite than for diamond. Therefore, the two curves must intersect at a pressure $p_{\alpha\beta}$, which we will call the transition pressure. The index αβ indicates that the transition of one modification α (here graphite) into another modification β (here diamond) is considered. Below $p_{\alpha\beta}$, graphite is more stable; above it, diamond is more stable.

The pressure $p_{\alpha\beta}$ can be calculated because $p_{\alpha\beta}$ is the pressure for which

$$\mu_\alpha = \mu_\beta. \tag{5.11}$$

The pressure dependence of μ is expressed by a linear relation,

$$\mu_{\alpha,0} + \beta_\alpha \cdot (p_{\alpha\beta} - p_0) = \mu_{\beta,0} + \beta_\beta \cdot (p_{\alpha\beta} - p_0),$$

resulting in

$$\mu_{\alpha,0} - \mu_{\beta,0} = -(\beta_\alpha - \beta_\beta) \cdot (p_{\alpha\beta} - p_0)$$

and finally

$$p_{\alpha\beta} = p_0 - \frac{\mu_{\alpha,0} - \mu_{\beta,0}}{\beta_\alpha - \beta_\beta} = p_0 - \frac{\mathcal{A}_0}{\beta}. \tag{5.12}$$

The expression shows a great formal similarity to the one for determining a transformation temperature whether it applies to a phase transition, a decomposition, or something else.

Inserting the tabulated values results in $p_{\alpha\beta} \approx 14 \times 10^5$ kPa (= 14,000 bar). Strictly speaking, this result cannot be accurate because the linear relations only represent approximations. However, as a general tool for orientation, it is quite useful.

5.4 Simultaneous Temperature and Pressure Dependence

There is nothing stopping us from expanding our ideas to transformations in which temperature *and* pressure change simultaneously. In this case the chemical potential can be expressed as follows:

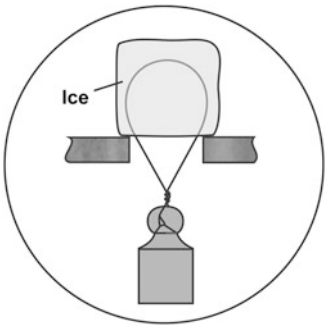
$$\mu = \mu_0 + \alpha \cdot (T - T_0) + \beta \cdot (p - p_0). \tag{5.13}$$

Correspondingly, the chemical drive takes the form

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T - T_0) + \beta \cdot (p - p_0). \tag{5.14}$$

The dependence of transition temperatures upon pressure can be described by these equations as well. Here is a familiar example representative of many others. Ice

Experiment 5.5 *Ice melting under pressure*: A wire loop with a heavy weight hanging from it slowly "melts" its way through a block of ice. The process is supported by the high entropy conductivity of the steel wire (see Sect. 20.4). The water formed below the wire under high-pressure flows around the wire and freezes again above it because of the lower pressure there. The ice block will remain intact even after the wire passes completely through.



melts under high pressure [if it is not too cold]. The chemical potential of ice is the same as that of ice water ($\mu(H_2O|s) = \mu(H_2O|l)$) at 273 K (0 °C) and standard pressure. However, because of $\beta(H_2O|s) > \beta(H_2O|l)$, the value of $\mu(H_2O|s)$ increases above that of $\mu(H_2O|l)$ as the pressure increases, and the ice begins to melt (Experiment 5.5).

As mentioned, water is among the few exceptions where β in the solid state is greater than in the liquid state. This special characteristic of ice is responsible for the ability of a glacier to flow downward a few meters per day in a mountain valley like slow moving dough. Where the ice is under especially high pressure, it melts and becomes pliable so that it gradually moves around obstacles.

But a block of ice does not totally melt when compressed because it cools down during melting. The reason for the drop in temperature is that the entropy required for the phase transition solid → liquid is not supplied from outside (cf. Sect. 3.5). It has to be provided by the system itself, leading to a lowering of temperature. The chemical potentials increase because of the negative temperature coefficients α. Because of $\alpha(H_2O|l) < \alpha(H_2O|s) < 0$, the effect is stronger in water than in ice. The potential difference due to excess pressure is compensated and the process of melting stops. Again, there is equilibrium between the solid and the liquid phase, but this time at a lower freezing point. Only when the pressure is further increased does the ice continue to melt until additional cooling balances the potentials again.

To illustrate this, let us take a look at Fig. 5.9. If the pressure is increased, the chemical potentials of the solid and the liquid phase increase, but this increase is much more pronounced for the solid than for the liquid phase [because of $0 < \beta(B|l) < \beta(B|s)$]. Thus the intersection point of the curves (T'_{sl}) shifts to the left, i.e., the freezing point is lowered by ΔT_{sl}.

It is easy to calculate the lowering of temperature in compressed ice, i.e., the freezing-point depression of water under pressure. The condition for equilibrium $\mu_s = \mu_l$ takes the following form:

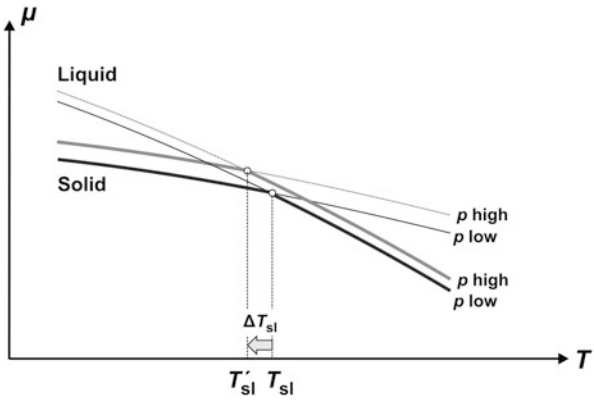


Fig. 5.9 Temperature dependence of the chemical potentials of a solid and a liquid phase at different pressures (in case of $0 < \beta_l < \beta_s$). The intersection point of the $\mu(T)$ curves at the pressure considered and hence the freezing-point shifts with increasing pressure to lower temperatures (lowering of freezing point).

$$\mu_{s,0} + \alpha_s \cdot (T - T_0) + \beta_s \cdot (p - p_0) = \mu_{l,0} + \alpha_l \cdot (T - T_0) + \beta_l \cdot (p - p_0)$$

or shortened:

$$\mu_{s,0} + \alpha_s \cdot \Delta T + \beta_s \cdot \Delta p = \mu_{l,0} + \alpha_l \cdot \Delta T + \beta_l \cdot \Delta p.$$

If the freezing point of water at standard pressure ($T_0 = 273$ K) is chosen as the initial value, then $\mu_{s,0}$ and $\mu_{l,0}$ are equal and drop out of the expression. The following relation remains with the change in temperature ΔT as the only unknown:

$$\Delta T = -\frac{\beta_s - \beta_l}{\alpha_s - \alpha_l} \Delta p = -\frac{\beta}{\alpha} \Delta p. \tag{5.15}$$

For $\Delta p = 10^4$ kPa (100 bar), the lowering of the freezing point due to pressure results in $\Delta T = -0.67$ K (calculated with the numerical values for ice and liquid water from Tables 5.1 and 5.2).

However, for most substances, the melting temperature increases with increased pressure [because of $0 < \beta(\mathrm{B}|\mathrm{s}) < \beta(\mathrm{B}|\mathrm{l})$] (see Fig. 5.10). Correspondingly, the shifts in potentials cause higher pressure to raise the boiling point and lower pressure to lower the boiling point [because of $0 < \beta(\mathrm{B}|\mathrm{l}) << << \beta(\mathrm{B}|\mathrm{g})$]. This is also valid for water as we have seen in Experiments 5.3 and 5.4. Again, the change ΔT can be approximated with the formula derived above. The value of β for boiling is roughly 10^4 times greater than for melting, whereas the α values do not vary so drastically. Therefore, even small changes of pressure are enough to noticeably shift the boiling point. To achieve a comparable change of the freezing point, much higher pressures are necessary. A pressure increase of about 10 kPa (0.1 bar) already results in a shift of the boiling point of water of about +2.0 K, while for a comparable change of the freezing point ($\Delta T = -2.0$ K), a pressure increase of more than 3×10^4 kPa (300 kbar) is necessary.

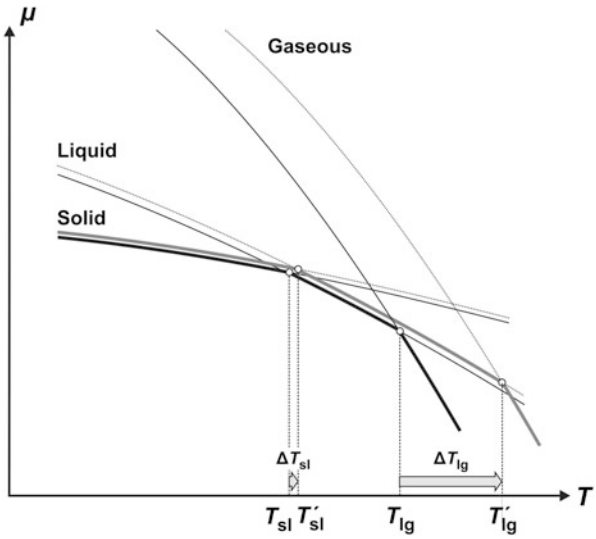


Fig. 5.10 Temperature dependence of the chemical potentials of a substance in solid, liquid, and gaseous states at low pressure (*lower curves*) and at high pressure (*upper curves*) (in case of $0 < \beta_s < \beta_l <<<< \beta_g$). The intersection points of the $\mu(T)$ curves and hence the freezing- and boiling-point shift with increasing pressure to higher temperatures (raising of freezing and boiling point).

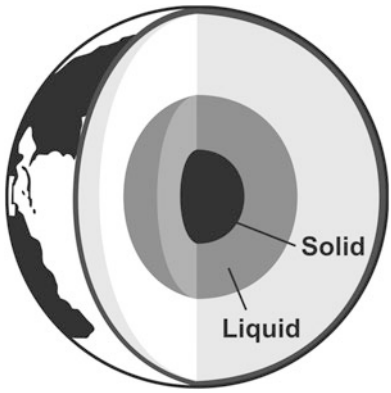


Fig. 5.11 Opposing effects of temperature and pressure in the Earth's interior: The temperature increase toward the middle of the Earth ($> 5{,}000$ K) causes the iron core to melt. The pressure, which grows to 3.6×10^8 kPa, turns it into a solid again at the very center (standard melting and boiling points of iron are about 1,809 and 3,340 K, respectively).

We will close this section with a look at our "home planet." It represents a very good example for the effect of increasing pressure and temperature upon the chemical potential and therefore the melting and freezing of substances (Fig. 5.11).

5.5 Behavior of Gases Under Pressure

As already stated, the chemical potential of gases is especially sensitive to changes of pressure. For this reason, the pressure coefficient β is greater by several powers of ten than those of solid or liquid substances. At the same time, β itself is strongly dependent upon pressure. For these reasons, the linear approximation is only applicable to a very narrow range of pressures $(\Delta p/p < 10\,\%)$. This is far too limiting for most applications so a formula must be sought that spans a much wider range of pressures. A look at the tabulated values shows that β has not only a large value but the same value for all gases at standard conditions. Apparently, the pressure coefficient β of gases is a *universal* quantity. For given T and p, it is the same for all gases in all milieus. Moreover, it is directly proportional to the absolute temperature T and indirectly proportional to the pressure p of the gas in question. This remarkable fact can be expressed as follows:

$$\beta = \frac{RT}{p} \quad \text{where } R = 8.314\ \mathrm{G\,K^{-1}}. \tag{5.16}$$

R is a fundamental constant and is the same for all substances. It is called the "(*general*) *gas constant*" because it was first discovered in a law valid for gases (Sect. 10.2). The relation above is based upon the phenomenon called *mass action* in chemistry. We will go more deeply into this in the next chapter. (Note: β corresponds here to the molar volume of a so-called ideal gas, as we will see in Sect. 10.2).

Inserting β into the relation (5.8) yields the following equation:

$$\mu = \mu_0 + \frac{RT}{p} \cdot (p - p_0). \tag{5.17}$$

Those proficient in mathematics immediately see that there is a logarithmic relation between μ and p:

$$\mu = \mu_0 + RT \ln \frac{p}{p_0}. \tag{5.18}$$

The pressure coefficient β of gases is nothing other than the derivative of the function $\mu(p)$ with respect to p. If we take the derivative with respect to p of the function above, we retrieve indeed Eq. (5.16).

For those interested in mathematics: Equation (5.17) can be transformed to result in

$$\mu - \mu_0 = \frac{RT}{p} \cdot (p - p_0) \quad \text{or} \quad \Delta\mu = \frac{RT}{p} \cdot \Delta p.$$

For very small (infinitesimal) changes, the relation is

$$\mathrm{d}\mu = \frac{RT}{p}\mathrm{d}p.$$

If we wish to calculate the change of the chemical potential from the initial value μ_0 to the final value μ for a change of pressure from p_0 to p, we must integrate both sides. (The concept of integration will be described in more detail in Sect. A.1.3 in the Appendix.) The following elementary indefinite integral will serve well for this:

$$\int \frac{1}{x}\,\mathrm{d}x = \ln x + \text{constant}.$$

Inserting the limits results in:

$$\int_{\mu_0}^{\mu} \mathrm{d}\mu = RT \int_{p_0}^{p} \frac{1}{p}\,\mathrm{d}p$$

and finally,

$$\mu - \mu_0 = RT \ln \frac{p}{p_0}.$$

We tend to consider a logarithm as unfamiliar and therefore complicated. This is unjustified. Basically, the relation is as simple as a linear one (cf. Sect. A.1.1 in the Appendix). In contrast to the linear approximation, this still relatively simple logarithmic formula spans the much wider range of pressures from between 0 and 10^4 kPa (100 bar). The range of validity will be discussed in more detail in Sect. 6.5.

Let us take a closer look at these relations using the example of butane (the fuel in a gas lighter) (Fig. 5.12). The $\mu(p)$ curve of gaseous butane shows the expected logarithmic relationship [cf. Eq. (5.18)]. Furthermore, we can see from the figure that, when compressed at room temperature, butane turns into liquid relatively easily. The so-called boiling pressure p_{lg}, i.e., the intersecting point of the potentials for the liquid and the gaseous phase, lies only a little above 200 kPa. This intersecting point characterizes the state of butane in a lighter at room temperature. However, further important information can be derived from the figure: The $\mu(p)$ curve for a liquid is an almost horizontal line. (Its slope is very small.) For this reason, the chemical potential of condensed phases (liquids and solids) can be considered nearly independent of pressure in most cases when they are present together with a gas. Furthermore, the chemical potential of a gas continues to decrease with falling pressure. The μ value approaches negative infinity if the pressure approaches zero.

This leads to the following remarkable conclusions. We can infer, for example, that calcium carbonate $CaCO_3$ cannot be stable if the CO_2 pressure in the surroundings falls to zero. In this case, the chemical potential of CO_2 would have the value $-\infty$. The reaction

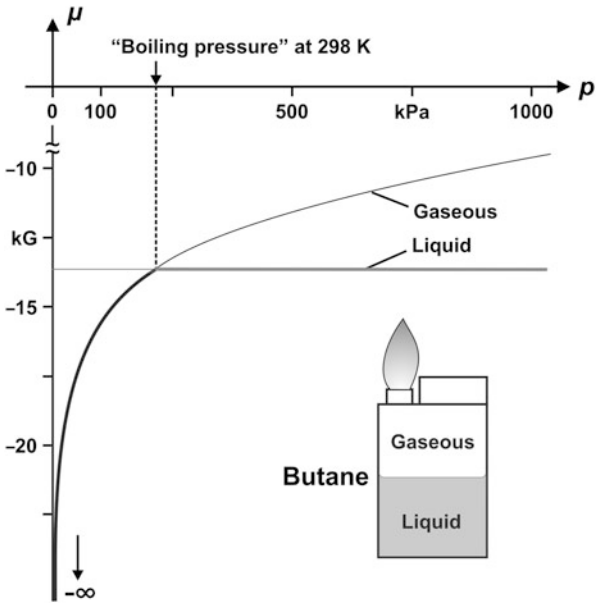


Fig. 5.12 Pressure dependence of the chemical potential of butane in liquid and gaseous states at room temperature (298 K).

	$CaCO_3\|s \rightarrow$	$CaO\|s$	$+ CO_2\|g$	
$\mu^{\ominus}$(kG):	−1128.8	−603.3	−394.4	$\Rightarrow \mathcal{A}^{\ominus} = -131.1$ kG
α (G K^{-1}):	−93	−38	−214	$\Rightarrow \alpha = +159$ G K^{-1},

which cannot take place at standard conditions, would have a positive drive. The sum of potentials on the left would be higher than on the right. However, decomposition produces CO_2, so that the CO_2 pressure must rise in a *closed* system. The process continues until the CO_2 pressure has reached a value for which the chemical potentials on the left and right sides balance. This CO_2 pressure is called the *decomposition pressure* of calcium carbonate.

The decomposition pressure can be easily calculated. If the chemical potentials satisfy

$$\mu_{CaCO_3} = \mu_{CaO} + \mu_{CO_2}$$

we have equilibrium. We ignore the pressure dependence of solid substances because, in comparison to gases, it is smaller by three orders of magnitude. We only take the dependence for CO_2 into account, and that at first for $T = T_0$:

$$\mu_{CaCO_3,0} = \mu_{CaO,0} + \mu_{CO_2,0} + RT\ln\frac{p}{p_0}.$$

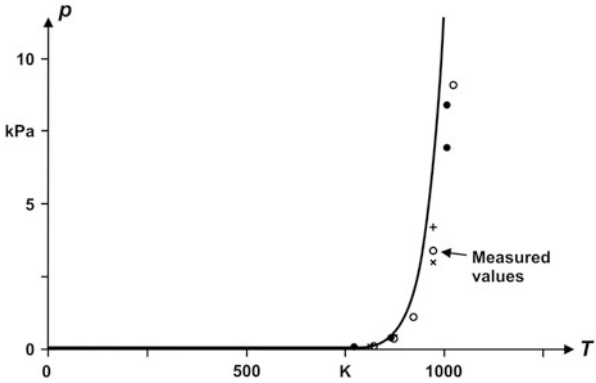


Fig. 5.13 Dependence of CO_2 pressure upon temperature during decomposition of calcium carbonate (comparison of the calculated curve with measured values).

This results in

$$\underbrace{\mu_{CaCO_3,0} - \mu_{CaO,0} - \mu_{CO_2,0}}_{\mathcal{A}_0} = RT \ln \frac{p}{p_0}$$

as well as

$$\exp \frac{\mathcal{A}_0}{RT} = \exp\left(\ln \frac{p}{p_0}\right)$$

and finally in the following exponential relation:

$$p = p_0 \exp \frac{\mathcal{A}_0}{RT}. \tag{5.19}$$

In order to calculate the decomposition pressure for a temperature different from the initial temperature T_0, the μ values in the exponents only need to be converted to the new temperature. The linear formula for temperature dependence used so far is generally good enough for this:

$$p = p_0 \exp \frac{\mathcal{A}_0 + \alpha(T - T_0)}{RT}.$$

With the help of corresponding data, i.e., the standard values and the corresponding temperature coefficients from Sect. A.2.1 in the Appendix, the $p(T)$ curve can be determined (Fig. 5.13). This curve gives the decomposition pressure of calcium carbonate as a function of temperature:

$$p = 100\,\text{kPa} \cdot \exp \frac{-1.311 \times 10^5 + 159 \cdot (T/\text{K} - 298)}{8.314 \cdot T/\text{K}}.$$