
Introduction

In the previous chapter, it was discussed the thermodynamics principles that are the basis of thermochemistry. It was shown how to calculate the energy involved in any chemical or physical transformation. Additionally, it was established the Gibbs free energy as a criterion to know whether or not such transformations would take place under a given set of conditions.

Furthermore based on the sign of the enthalpy change associated to any of these transformations, it is possible to distinguish if we need to supply heat to the system or to withdraw it.

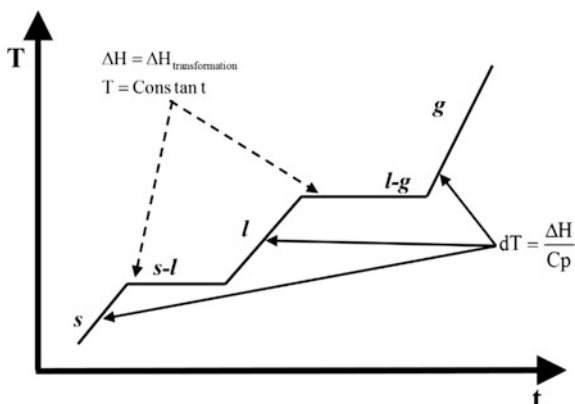
As chemical reactions occur, they occasionally involve phase transitions such as allotropy, melting, boiling, etc. As they take place, their requirement of energy can be easily accounted, but more importantly, it is possible to relate such energy demands to determine specific conditions under which two or more phases can coexist simultaneously in equilibrium.

Heat and Phase Changes

To boil water, it is necessary to provide heat, as heat is supplied to the liquid, the water temperature increases in inverse proportion to the heat capacity of the liquid.

This happens until the normal boiling point of the liquid is reached. At that point, boiling begins and the temperature of the water remains constant while the heat supplied to the system boils the liquid. The water temperature does not increase again until all the liquid has fully transformed into vapor. Once the liquid has disappeared, the temperature of the system again increases, this time in inverse proportion to the heat capacity of the gas. If we plot this experiment over a wide enough range of temperature to go from solid to liquid to vapor, the plot would look something like Fig. 2.1.

Fig. 2.1 Heat exchange during heating of a substance, phase transformations occur at constant temperature



In such plot, time directly relates to the energy supplied in the form of heat since it is assumed that heat is added at a constant rate. This graph is somewhat idealistic; the slopes (temperature increase) for the solid, liquid and gas will not be equal (each slope will be the inverse of the heat capacity for that particular phase) nor will they be linear since we know that heat capacity increases with temperature. Still, over a short enough range, the heat capacities of each phase can be assumed as constant.

The heat that must be supplied to convert one phase into another (solid to liquid, liquid to vapor) is just the enthalpy of the phase transition (ΔH_{fusion} , $\Delta H_{\text{vaporization}}$, etc.), adjusted appropriately for the number of moles of substance present at the moment of the transformation. Because this amount of energy has to be supplied to the lower temperature phase to convert it into the higher temperature phase, it is called the latent heat of the phase transition.

For phase transitions with latent heat, the corresponding entropy of the phase change is:

$$\Delta S_{\text{transformation}} = \frac{\Delta H_{\text{transformation}}}{T_{\text{transformation}}} \quad (2.1)$$

Phase transitions with latent heats are called first-order transitions. The phase jump from one state to the other is discontinuous with temperature. In second-order transition, such as the demagnetization of iron, the change is continuous over a range of temperatures.

Gibbs Rule of Phases

Chemical systems are made of elements and/or molecules whose masses cannot be taken arbitrarily; there exist certain mass relationships among them. For example, if we have a system with magnesium carbonate, magnesium oxide and carbon dioxide, the system is composed of C, Mg, and oxygen. We can randomly pick the

mass of two of these elements, but the third one will be determined by itself without any doubt. Thus, it is possible to choose in many different ways the number of components (C) in any system.

On the other hand, we usually face heterogeneous systems. In general, it is quite simple to enumerate the distinct phases that are present in a given system. For example, a system formed by liquid water and water vapor has two phases. A system containing salt crystals and an aqueous solution of this salt has likewise two phases (the salt and the solution). In general, the number of phases comprising a system is denoted by (P). It is clear now that any system is characterized by the number of components (C) and that of the phases (P) into which the system is divided.

If we define process variables (temperature, pressure, composition) of each phase within the system, then it is possible to estimate the number of physical variables that can be changed, without varying the number of phases present. The number of process variables to change is known as degrees of freedom (F) and these are related to the number of components and phases by:

$$F = C - P + 2 \quad (2.2)$$

Equation (2.2) is known as Gibbs rule of phases.

One Component Systems

If we plot the pressure versus the temperature for an element or a molecule like water, the system is comprised by a single component; such diagram, like the one sketched in Fig. 2.2, reveals phase stability regions as well as phase boundaries. As we know, water can exist as solid, liquid or gas, therefore fields corresponding to these phases are properly labeled in the diagram, we also know that depending on atmospheric or process conditions two of these phases can coexist, like ice and water in a pond during wintertime or steam and liquid water in dry cleaning shops. The phases can coexist along the lines (boundaries) delimiting them. Also, there is a well-defined point in which the three phases can coexist; this point is named the triple point. This triple point is unique for each system/compound.

Direct application of Gibbs rule of phases (Eq. 2.2) to any unary system represented in a pressure—temperature (PT) diagram, results in (Table 2.1).

In those regions containing any of the S , L or G phases, we have two degrees of freedom which means that both pressure and temperature can vary freely, without altering the corresponding phase. Along phase boundaries, there is only one degree of freedom; this means that along any of these lines we can define arbitrarily either the pressure or the temperature; then the second variable will be fixed by itself. At the triple point, the three phases coexist in equilibrium; this means that there is a specific P-T combination at which the phases can be present simultaneously. Thus, at this point there are no degrees of freedom.

Fig. 2.2 Pressure—
temperature diagram for water
(schematic)

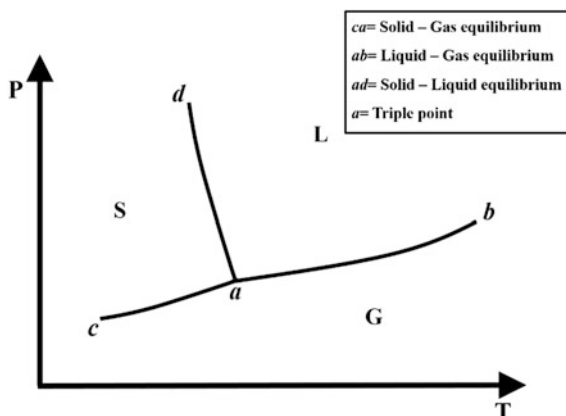


Table 2.1 Gibbs rule of
phases in mono component
systems

Region in P-T diagram	C	P	F
Phase field	1	1	2
Phase boundary	1	2	1
Triple point	1	3	0

Since it is possible for the different phases to coexist, then we should be able to relate the free energy of each phase in a way to find correlations between process variables and the corresponding energy change.

Thermodynamics of One Component Systems

In Chap. 1, it was shown that it is possible to express Gibbs free energy as a function of temperature and pressure:

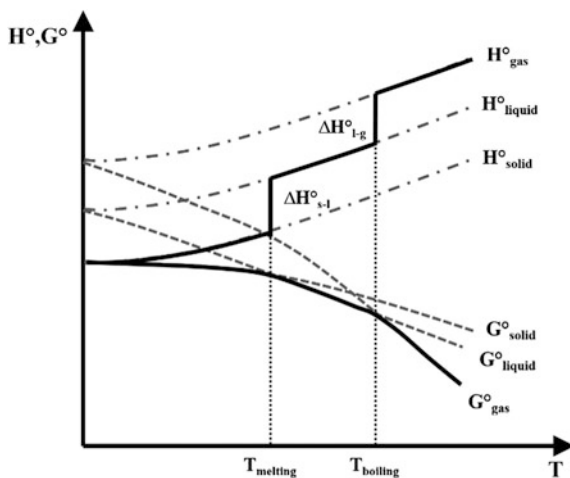
$$dG = VdP - SdT. \quad (1.27)$$

Taking partial derivatives of expression (1.27) with respect of pressure and temperature; the following relationships are obtained:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (2.3a)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V. \quad (2.3b)$$

Fig. 2.3 Gibbs free energy and enthalpy changes for phases in equilibrium as a function of temperature



Plotting G and H for each phase at constant pressure, show that as temperature increases, Gibbs free energy of each phase becomes more negative, and the most stable phase at higher temperature is the one with larger specific heat, this is illustrated in Fig. 2.3.

As seen in Fig. 2.3, the free energy curve can be crossed in more than one occasion this lead to entropy ratios $\frac{S_{\text{phase2}}}{S_{\text{phase1}}}$, these ratios are larger than unity and increase as temperature does. This confirms the effect of temperature on the free energy. As temperature increases, the entropy contribution to ΔG becomes more important. Furthermore if we follow phase transitions as more energy is supplied to any system, we can easily observe the change of entropy as a solid transforms into a liquid and the liquid boils into a gas. Not surprisingly, the entropy of each phase progressively increases from the solid to the gaseous state; this can be seen in Fig. 2.4.

Clapeyron Equation

Figures 2.3 and 2.4 show the effect of enthalpy and entropy, respectively, on Gibbs free energy during phase transitions. With this, it is possible to associate this free energy to any of the phase boundaries in Fig. 2.2. To do so, we need to equate the free energy of the phases in equilibrium. For example, consider a solid—gas equilibrium. We can represent such equilibrium as a chemical reaction:



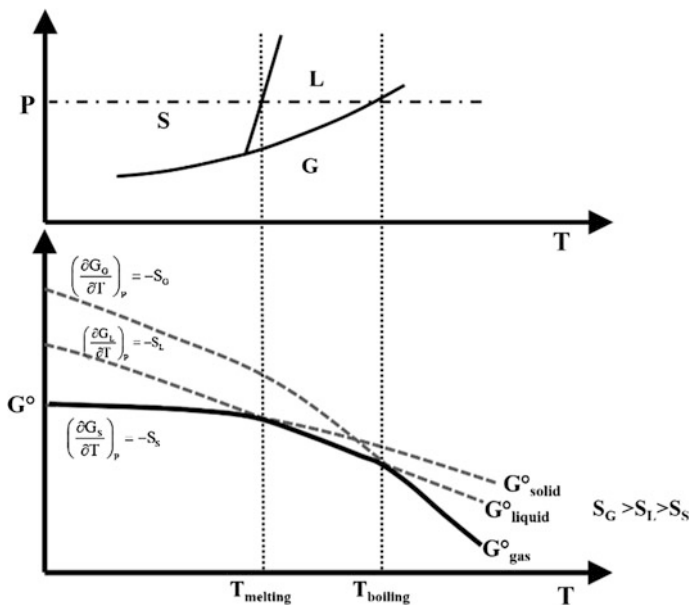


Fig. 2.4 Effect of entropy on Gibbs free energy during phase transitions

From Eq. (2.4), we have that at the phase boundary; the corresponding free energies are equated:

$$G_S = G_L \quad (2.5)$$

Substituting Eq. (1.27) into (2.5), results in:

$$V_S dP - S_S dT = V_L dP - S_L dT. \quad (2.6)$$

Accommodating terms in expression (2.6)

$$G_S - G_L = (V_S - V_L)dP - (S_S - S_L)dT. \quad (2.7)$$

Since at the phase boundary both phases are in equilibrium, then $G_S - G_L$ should be zero, therefore, Eq. (2.7) can be written as:

$$\Delta G_{S-L} = \Delta V_{S-L}dP - \Delta S_{S-L}dT = 0. \quad (2.8)$$

From Eq. (2.8), we have:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \quad (2.9)$$

Equation (2.9) is known as Clapeyron equation. This equation can be modified if we substitute expression (1.11) into (2.9), to obtain:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}. \quad (2.9a)$$

Clapeyron equation applies to any phase change in a one-component system. This equation, only determines the slope of the equilibrium boundary, not the actual position of the reaction in the pressure–temperature domain. That position must be determined by further thermodynamic calculations or by experiments.

For example, a reaction with shallow dP/dT slope is more sensitive to pressure changes, whereas a reaction with a steep (nearly vertical) slope is sensitive to temperature.

Additionally, if we collect experimental data on any reaction at a given temperature (or pressure), we can determine the slope and extrapolate to other conditions, rather than doing more time-consuming experiments.

Clapeyron equation helps determining thermodynamic values for reactions or phases. When combined with volume data, we can use the slope of an experimentally determined reaction to calculate the entropy change of the reaction, and to calculate the entropy of formation of a particular phase. Often the volume of a phase is well known, but the entropy data may have considerable uncertainties.

In some instances, volume changes are quite large, especially if a gas phase is involved in the transformation we are interested in, thus the ΔV term in Clapeyron equation can be assumed as the volume of the gas phase; by doing so, we can modify Eq. (2.9) using the ideal gas equation, resulting in:

$$\frac{dP}{dT} = \frac{\Delta H}{RT^2} P. \quad (2.10)$$

Variable separation in expression (2.10) results in:

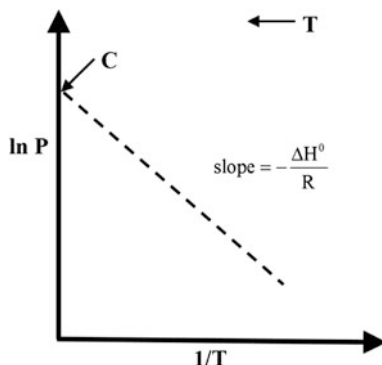
$$\frac{dP}{P} = \frac{\Delta H}{R} \frac{dT}{T^2}. \quad (2.11)$$

Equation (2.11) is the differential form of Clausius—Clapeyron equation. Integration of this expression results in:

$$\ln(P) = -\frac{\Delta H}{R} \frac{1}{T} + C. \quad (2.12)$$

C is an integration constant that should be evaluated depending on the system properties. Clausius—Clapeyron equation can be applied to any phase transformation (melting, boiling, sublimation, allotropy). It is also worth noting that plotting $\ln(P)$ versus $(1/T)$, would yield a straight line whose slope is equal to $-\Delta H/R$; from this slope it can be calculated the enthalpy change associated to the transformation under

Fig. 2.5 Graphical representation of Clausius—Clapeyron equation



study. The intersection of this line with the $\ln(P)$ axis will give the value of C constant. This is illustrated in Fig. 2.5.

Equation (2.11) can also be integrated between limits P_1 and P_2 corresponding to T_1 and T_2 , respectively; if such is the case, Eq. (2.12) results in:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right). \quad (2.13)$$

This last expression is the integrated form of Clausius–Clapeyron equation. Relation (2.13) is often used to estimate the vapor pressures of pure liquids or solids. ΔH is the enthalpy of vaporization if the substance is a liquid or the enthalpy of sublimation if it is a solid. The enthalpy of vaporization (or sublimation) is assumed to be constant over the temperature range of interest. This is not true, but actual changes in ΔH values are negligible at low and moderate pressures. The vapor phase can be assumed as an ideal gas, since the external pressure does not significantly affect its pressure.

On the other hand, and in order to simplify calculations, the latent heat of evaporation can be estimated using Trouton's rule. This rule states that the ratio of latent heat of evaporation to the normal point is constant for many liquids:

$$\frac{\Delta H_{\text{vap}}^\circ}{T_{\text{vap}}} = 88 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (2.14)$$

This rule is an approximate one. However, it is useful to estimate near values for the heat of evaporation. Data in Fig. 2.6 from Kubaschewski and Alcock¹ reveal the departure from this law, especially at higher boiling points.

The departure from Trouton's rule can be explained by the presence of several gaseous species during boiling; for example, when PbF_2 boils, its vapor not only

¹Kubaschewski, O., Alcock, C.B., Metallurgical Thermochemistry 5th Ed., Pergamon Press, Oxford, 1979.

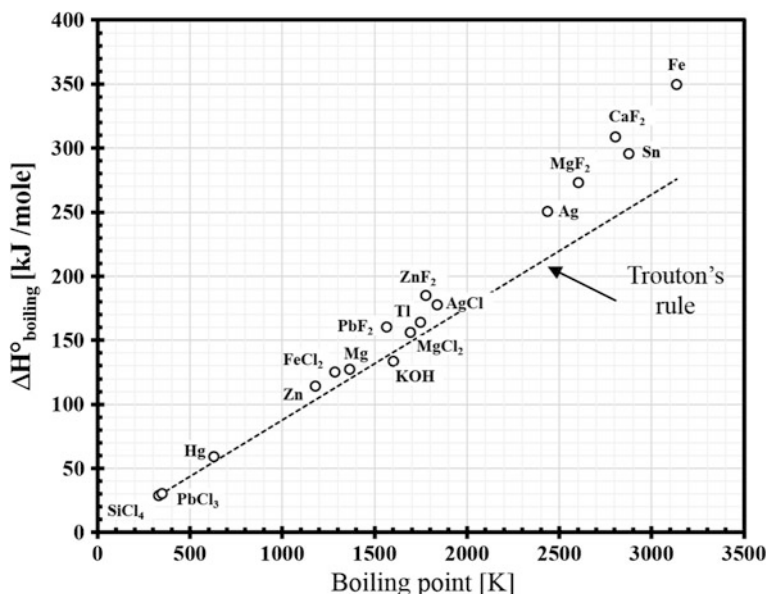


Fig. 2.6 Trouton's rule and deviation from this rule of some elements and compounds. Data from Kubaschewski and Alcock

contains such fluoride, but also contains minor amounts of other species such as PbF, PbF₄, and Pb.

In some applications, it is important to know the vapor pressure of metals and alloys. Vapor of solids or liquids results from the dissociation of the substance in the gaseous state as a consequence of thermal movement of atoms or molecules. Vaporization is a reversible process highly sensitive on temperature; a small variation in temperature produces condensation of the vapor phase. Therefore, vaporization strongly depends on the pressure and temperature to which the system is kept.

The enthalpy of vaporization $\Delta H^\circ_{\text{vap}}$ is equal in magnitude but opposite in sign to the enthalpy of condensation; however, the value of the enthalpy of vaporization changes with the temperature. Furthermore, it has been observed that $\Delta H^\circ_{\text{vap}}$ increases with the atomic weight (mass).

Using Calusius—Clapeyron equation (Eq. 2.11) to relate the vapor pressure of metals or alloys to the temperature:

$$\frac{dP}{P} = \frac{\Delta H^\circ_{\text{vap}}}{R} \frac{dT}{T^2}. \quad (2.11)$$

Integration between limits P_1 , P_2 and T_1 , T_2 yields Eq. (2.13); setting P_1 as 1 atmosphere and T_1 as the boiling point (T_{boiling}) and approximating using Trouton's rule (Eq. 2.14):

$$\ln(P_2) - \ln(1) = \frac{\Delta H_{\text{vap}}^{\circ}}{RT_{\text{boiling}}} - \frac{\Delta H_{\text{vap}}^{\circ}}{RT_2}. \quad (2.15)$$

Reduces to:

$$\ln(P_2) = \frac{88}{8.314} - \frac{\Delta H_{\text{vap}}^{\circ}}{RT_2}. \quad (2.15a)$$

It is customary to represent vapor pressure data in terms of the log function rather than the ln one, thus, Eq. (2.15a) has to be altered by a factor of 2.303:

$$\log(P_2) = 4.6 - \frac{\Delta H_{\text{vap}}^{\circ}}{19.147T_2}. \quad (2.15b)$$

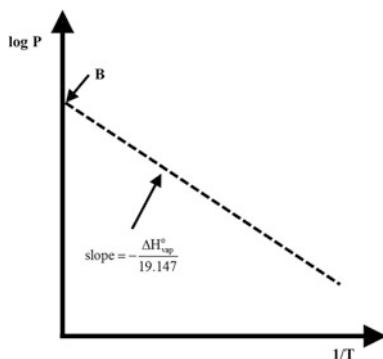
This last result allows for a good approximation of the vapor partial pressure of a metal or alloy; additionally it is evident that vapor pressure data can be estimated by a general relation:

$$\log P = \frac{A}{T} + B. \quad (2.16)$$

Plotting $\log P$ versus $1/T$ results in a straight line whose slope equals $-\Delta H_{\text{vap}}^{\circ}/19.147$. This is illustrated in Fig. 2.7.

If sublimation (solid transforming into a gas) takes place, a similar expression for the vapor pressure over a solid can be deduced. The entropy associated to sublimation can be assumed² as $96 \text{ J mole}^{-1} \text{ K}^{-1}$. With such value the following relation

Fig. 2.7 Relationship between $\log P$ and $1/T$



²Biswas A.K., Bashforth G.R., The Physical Chemistry of Metallurgical Processes, Chapman and Hall, London, 1962.

between the partial pressure of the solid and its enthalpy of sublimation $\Delta H_{\text{sub}}^\circ$ can be obtained:

$$\log P = -\frac{\Delta H_{\text{sub}}^\circ}{19.147T} + B'. \quad (2.17a)$$

Substituting the entropy of sublimation in (2.17a) gives:

$$\log P = 5.0 - \frac{\Delta H_{\text{sub}}^\circ}{19.147T}. \quad (2.17b)$$

Therefore knowing the vapor pressure expression for the liquid phase, the melting point and the heat of fusion it is then possible to obtain a general equation valid for the solid phase; moreover, it is then concluded the validity of the following relation:

$$\Delta H_{\text{sub}}^\circ = \Delta H_{\text{vap}}^\circ + \Delta H_{\text{fusion}}^\circ. \quad (2.18)$$

Example of Calculations

Example 1 Gibbs rule of phases

Part (A)

An equimolar mixture of H_2 and O_2 is contained in a pressurized cylinder. A spark causes a reaction resulting in the formation of water droplets. List the degrees of freedom before and after the water forming reaction.

Solution

In this case we have a gaseous mixture (1 phase, two components) transforming chemically into 1 phase and one component.

Gibbs rule of phases: $F = C - P + 2$

$\text{H}_2 + 0.5 \text{ O}_2$			H_2O		
C	P	F	C	P	F
2	1	3	1	1	2

Part (B)

Evaluate P, C and F for each of the following systems/reactions:

- A mixture of five gases enclosed in a cylinder
- $2\text{HI} = \text{H}_2 + \text{I}_2$ in vapor phase, starting with various mixtures of hydrogen and iodine

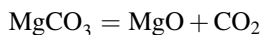
- c. H_2 , O_2 and H_2O enclosed in a vessel at room temperature
- d. $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$ at high temperature starting with water
- e. Solid carbon, CO , CO_2 and O_2 in equilibrium at 600°C
- f. $(\text{CH}_3\text{COOH})_2 \text{ liquid} = (\text{CH}_3\text{COOH})_2 \text{ gas}$

Solution

System	C	P	F	Comments
a	5	1	6	This is a gaseous solution with 5 components. No chemical interaction between components
b	2	1	3	This systems considers the decomposition of HI into H_2 and I_2 gases; therefore there are two components mixed in one phase
c	3	2	3	At room temperature liquid water is the most stable phase. This is in equilibrium with a gaseous mixture made of H_2 and O_2
d	1	1	2	In this case water is expected to be in the gaseous phase, therefore there are 3 components mixed together in a single phase
e	4	2	4	Two phases (1 solid, 1 gas) coexist. 3 components are present in the gas and 1 component in the solid
f	1	2	1	There is a single component existing in two distinct phases

Part (C)

At high temperature, magnesium carbonate dissociates and can exist in equilibrium with the decomposition products:



- (a) State the number of phases and components in this system
- (b) Would the number of components be changed by adding CO_2 from an external source?
- (c) Would the number of phases be altered?

Solution

- (a) At equilibrium, there are 3 phases, 2 solids (MgCO_3 and MgO) and one gas (CO_2). The number of components is also 3, the carbonate, the oxide and the gas.
- (b) No it would not change, since CO_2 is already in the system.
- (c) No, because CO_2 is in the gas phase and already is in the system.

Part (D)

Ammonium chloride vaporizes upon heating.

- (a) State the number of components in a system consisting of solid ammonium chloride and its vapor
- (b) Would the number of components be changed by admitting ammonia gas into the system?
- (c) Would the number of phases be altered?
- (d) Would equilibrium be still possible?

Solution

- (a) There is one component (NH_4Cl) and two phases (1 solid, 1 gas)
- (b) Yes, there would be 2 components (NH_4Cl , NH_3)
- (c) No, there would still be a gaseous phase and a solid one
- (d) Yes, it would.

Example 2 Clausius—Clapeyron equation The vapor pressures of sodium are written as:

$$\log P = 10.304 - \frac{5603}{T} \quad (\text{E2.1})$$

and

$$\log P = 9.710 - \frac{5377}{T} \quad (\text{E2.2})$$

Where P is in Pa and T in K. Which of the two equations is for solid sodium?

Solution

We need to convert $\log P$ into $\ln P$ ($\ln P = 2.303 \log P$) in order to be able to use Clausius—Clapeyron equation:

$$\begin{aligned} \ln P &= 2.303 \left[10.304 - \frac{5603}{T} \right] \\ \ln P &= 23.730 - \frac{12903.709}{T} \end{aligned} \quad (\text{E2.1a})$$

and,

$$\begin{aligned} \ln P &= 2.303 \left[9.710 - \frac{5377}{T} \right] \\ \ln P &= 22.362 - \frac{12383.231}{T} \end{aligned} \quad (\text{E2.2a})$$

Using Clausius—Clapeyron Eq. (2.11) with the form:

$$\frac{d \ln P}{dT} = \frac{\Delta H_1^\circ}{RT^2} \quad (\text{E2.3})$$

Applying equation (E2.3) to expressions (E2.1a) and (E2.2a) results in:

$$\begin{aligned} \frac{d \ln P}{dT} &= \frac{d}{dT} \left(23.730 - \frac{12903.709}{T} \right) \\ \frac{d \ln P}{dT} &= \frac{12903.709}{T^2} = \frac{\Delta H_1}{RT} \end{aligned} \quad (\text{E2.1b})$$

and

$$\begin{aligned} \frac{d \ln P}{dT} &= \frac{d}{dT} \left(22.362 - \frac{12383.231}{T} \right) \\ \frac{d \ln P}{dT} &= \frac{12383.231}{T^2} = \frac{\Delta H_2}{RT} \end{aligned} \quad (\text{E2.2b})$$

From expressions (E2.1b) and (E2.2b) it is evident that $\Delta H_1 > \Delta H_2$, therefore, equation (E2.1) corresponds to solid sodium.

Example 3 Use of Clapeyron equation Calculate the pressure that must be applied to silver to increase its melting temperature by 10 and 20 K, using the following data:

Property	Value
Atomic mass (M)	107.87 g mole ⁻¹
Melting point (T _{fus})	961.8 °C
Solid density (ρ _s)	10.50 g cm ⁻³
Liquid density (ρ _l)	9.32 g cm ⁻³
Heat of melting (ΔH _{fus} ^o)	11280 J mole ^{-1s}

Solution

We need to calculate the molar volume of both solid and liquid silver:

$V_{\text{molar}} = \frac{M}{\rho}$; for each phase we have:

$$\begin{aligned} V_{\text{m,solid}} &= \frac{M_{\text{Ag}}}{\rho_{\text{Ag,s}}} = \frac{107.87 \frac{\text{g}}{\text{mole}}}{10.50 \frac{\text{g}}{\text{cm}^3}} = 10.27 \frac{\text{cm}^3}{\text{mole}} \\ V_{\text{m,liquid}} &= \frac{M_{\text{Ag}}}{\rho_{\text{Ag,l}}} = \frac{107.87 \frac{\text{g}}{\text{mole}}}{9.32 \frac{\text{g}}{\text{cm}^3}} = 11.57 \frac{\text{cm}^3}{\text{mole}} \end{aligned}$$

From these molar volumes, we can calculate the volume change due to silver melting:

$$\Delta V = V_{\text{m, liquid}} - V_{\text{m, solid}} = 11.57 - 10.27 = 1.3 \frac{\text{cm}^3}{\text{mole}} \quad \text{or} \quad 1.3 \times 10^{-6} \frac{\text{m}^3}{\text{mole}}$$

We can integrate Clapeyron’s equation between limits $1.01325 \times 10^5 \text{ Pa}$ at T_{fus} and P at T :

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta H}{\Delta V} \frac{1}{T} \\ \int_{1.01325 \times 10^5}^P dP &= \frac{\Delta H}{\Delta V} \int_{1234.8}^T \frac{dT}{T} \\ P &= \frac{\Delta H}{\Delta V} \ln\left(\frac{T}{1234.8}\right) + 1.01325 \times 10^5 \\ P &= \frac{11280}{1.3 \times 10^{-6}} \ln\left(\frac{T}{1234.8}\right) + 1.01325 \times 10^5 \end{aligned}$$

Substituting the corresponding temperature values (in K) in the last equation, we can calculate the pressure increase needed to melt silver:

T (°C)	P (atm)
961.8	1
971.8	691.7
981.8	1376.9
991.8	2056.6

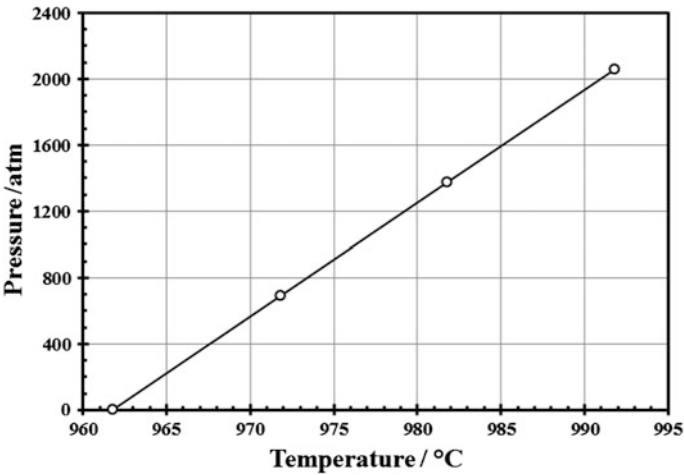
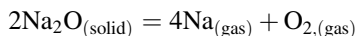


Fig. 2.8 Pressure increase to augment the meltinl g point of silver

The relationship between the temperature (°C) increase and the corresponding pressure (atm) increment is shown in the figure below (Fig. 2.8).

Example 4 Calculation of phase boundary line The dissociation of Na_2O at 1000 °C can be represented by:



For this reaction, $\Delta G^\circ_{1273} = 450.77 \text{ kJ}$. Graphically determine under which conditions, sodium oxide would not decompose:

Solution

For this problem, ΔG° is given, therefore we can relate the equilibrium constant to the partial pressures of the gases resulting from the oxide decomposition

$$\begin{aligned}\Delta G^\circ_{1273} &= -RT \ln(K) \\ K &= \exp\left(-\frac{\Delta G^\circ_{1273}}{RT}\right) = \exp\left(-\frac{450770}{8.314 \times 1273}\right) \\ K &= 3.18 \times 10^{-19}\end{aligned}$$

On the other hand, from the dissociation reaction we can express the equilibrium constant in terms of partial pressure of sodium and oxygen:

$$\begin{aligned}K &= p_{\text{O}_2} \times p_{\text{Na}}^4 \\ 3.18 \times 10^{-19} &= p_{\text{O}_2} \times p_{\text{Na}}^4\end{aligned}$$

The logarithm of the previous equation, allow us to express the partial pressure of sodium as a function of that of the oxygen evolving from the oxide:

$$\begin{aligned}\log(3.18 \times 10^{-19}) &= \log(p_{\text{O}_2}) + 4 \log(p_{\text{Na}}) \\ \log(p_{\text{Na}}) &= \frac{-18.5 - \log(p_{\text{O}_2})}{4}\end{aligned}$$

We can assign values to the partial pressure of oxygen so we can calculate the equilibrium value for that of sodium and thus define the equilibrium line between the oxide and its dissociation products; this is illustrated in the figure below (Fig. 2.9).

Example 5 Determination of the heat of sublimation of water using the heat of vaporization and that of melting along with Clasius–Clapeyron equation The heats of vaporization and of fusion of water are $45.054 \text{ kJ mole}^{-1}$ and $6.01 \text{ kJ mole}^{-1}$ at 0 °C, respectively. The vapor pressure of water at 0 °C is 0.006 atm. Calculate the sublimation pressure of ice at -15 °C, assuming that the enthalpies of transformation do not change with temperature.

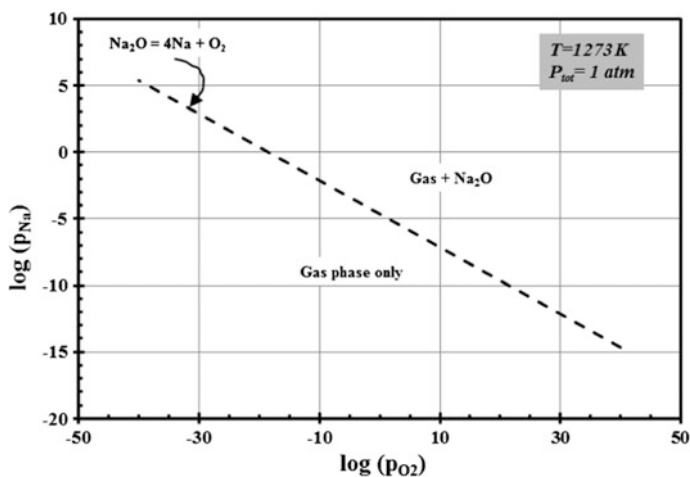


Fig. 2.9 Phase stability in the dissociation of Na_2O

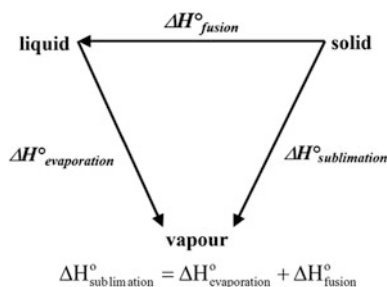


Fig. 2.10 Relationship between the standard heat of evaporation, sublimation and fusion

Solution

The heats of transformation are related as indicated in the sketch below. According to this figure, we can calculate the heat of sublimation of water at 0°C by combining the heats of evaporation and melting at the same temperature. With that heat, then we can use Clausius–Clapeyron equation to calculate the pressure for transforming solid water into vapor at -15°C (Fig. 2.10).

To calculate the heat of sublimation at 273 K , we can use Eq. (2.18):

$$\begin{aligned}\Delta H_{\text{sub},273}^\circ &= \Delta H_{\text{evap},273}^\circ + \Delta H_{\text{fus},273}^\circ \\ \Delta H_{\text{sub},273}^\circ &= 45.054 + 6.010 \text{ kJ mole}^{-1} \\ \Delta H_{\text{sub},273}^\circ &= 51.064 \text{ kJ mole}^{-1}.\end{aligned}$$

Assuming that this value is independent of temperature, we can calculate the sublimation pressure at a lower temperature:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\text{sub}}^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Solving for P_2 , and substituting the corresponding values:

$$\begin{aligned} P_2 &= P_1 \exp\left[-\frac{\Delta H_{\text{sub}}^{\circ}}{R}(T_2^{-1} - T_1^{-1})\right] \\ P_2 &= 0.006 \exp\left[-\frac{51064}{8.314}(258^{-1} - 273^{-1})\right] \\ P_2 &= 0.0017 \text{ atm.} \end{aligned}$$

As temperature drops 15 °C, the pressure to transform solid water into vapor decreases as well. This is observed in the P-T plot below (Fig. 2.11).

Example 6 Estimation of vapor pressure by combining Trouton's rule and Clausius–Clapeyron equation Mercury evaporates at 357 °C (630 K) under 1 atm of pressure. Calculate its approximate vapor pressure at 100 °C, assuming that it follows Trouton's rule.

Solution

First, we need to find $\Delta H_{\text{vap}}^{\circ}$ from Trouton's rule:

$$\begin{aligned} \frac{\Delta H_{\text{vap}}^{\circ}}{T_{\text{evaporation}}} &= 88 \text{ J mole}^{-1} \text{ K}^{-1}; \\ \Delta H_{\text{vap,Hg}}^{\circ} &= 88(T_{\text{evaporation,Hg}}) \\ \Delta H_{\text{vap,Hg}}^{\circ} &= 88(630) \\ \Delta H_{\text{vap,Hg}}^{\circ} &= 55440 \text{ J mole}^{-1}. \end{aligned}$$

Substituting this $\Delta H_{\text{vap,Hg}}^{\circ}$ value, into Clausius–Clapeyron equation, and solving for the gas pressure at the desired temperature:

$$\begin{aligned} \ln\left(\frac{P_2}{P_1}\right) &= -\frac{\Delta H_{\text{vap}}^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ P_2 &= P_1 \times \exp\left[-\frac{\Delta H_{\text{vap}}^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \\ P_2 &= 1 \times \exp\left[-\frac{55440}{8.314}\left(\frac{1}{373} - \frac{1}{630}\right)\right] \\ P_2 &= \exp[-7.293] \\ P_2 &= 0.0007 \text{ atm}; \quad P_2 = 70.9 \text{ Pa.} \end{aligned}$$

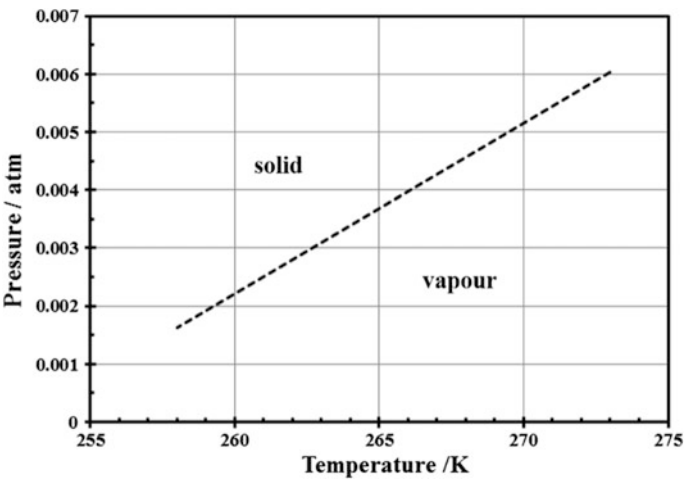


Fig. 2.11 Solid–vapor equilibrium for water

Example 7 Estimation of the heat of transformation from raw temperature and pressure data Calculate the mean heat of vaporization of palladium from the following data:

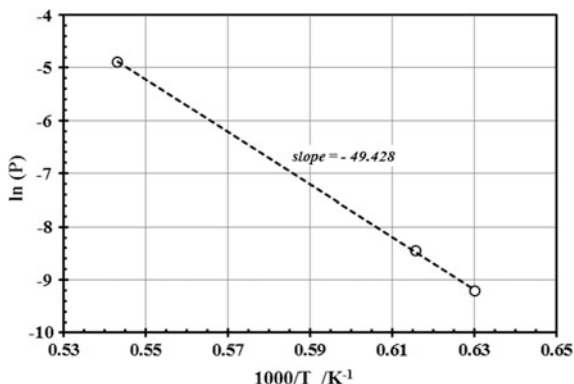
T (°C)	P (Pa)
1314	1.00×10^{-4}
1351	2.15×10^{-4}
1568	7.50×10^{-3}

Solution

To find the heat of vaporization, we need to work out the raw data to obtain the logarithm of the pressure and the inverse of the temperature in absolute scale, such manipulation results in:

P (Pa)	ln P	T (°C)	T (K)	$10^3/T$ (1/K)
1.00×10^{-4}	−9.210	1314	1587	0.630
2.15×10^{-4}	−8.445	1351	1624	0.616
7.50×10^{-3}	−4.893	1568	1841	0.543

Fig. 2.12 Vapor pressure of palladium as a function of the inverse of temperature



Accordingly with Clausius–Clapeyron equation, plotting $\ln(P)$ versus $10^3/T$, would result in a straight line whose slope is equivalent to $-\frac{\Delta H_{\text{vap}}^\circ}{R}$. By taking $10^3/T$, the resulting heat of evaporation will be expressed in kJ mole^{-1} . This is shown in (Fig. 2.12).

From the slope, the heat of evaporation of palladium becomes:

$$\begin{aligned}\Delta H_{\text{vap}}^\circ &= -\text{slope} \times R \\ \Delta H_{\text{vap}}^\circ &= 49.428 \times 8.314 \\ \Delta H_{\text{vap}}^\circ &= 411 \text{ kJ mole}^{-1}.\end{aligned}$$

Example 8 Use of Clapeyron and Clausius–Clapeyron equations to solve every day problems

Part (A)

How much a speed skater, who is 70 kg by weight, decreases the melting point of ice? The skating iron is 1 by 400 mm. Assume all his weight is on one skate at a time. Data: $\Delta S_{\text{fus}}^\circ = 21.97 \text{ J mole}^{-1} \text{ K}^{-1}$; $\Delta V_{\text{fus}} = -1.49 \text{ cm}^3 \text{ mol}^{-1}$.

Solution

For this problem, we need to use Clapeyron equation

$$\begin{aligned}\frac{dP}{dT} &\approx \frac{\Delta P}{\Delta T} = \frac{\Delta S_{\text{melting}}^\circ}{\Delta V_{\text{melting}}} \\ \Delta T &= \Delta P \frac{\Delta V_{\text{melting}}}{\Delta S_{\text{melting}}^\circ}\end{aligned}\tag{E7.1}$$

It is necessary to calculate the pressure exerted by the skater on the ice surface:

$$\Delta P = \frac{F}{A} = \frac{70 \times 9.8}{10^{-3} \times 0.4} = 1.715 \times 10^6 \text{ Pa}.\tag{E7.2}$$

Substituting this pressure value into equation (E7.1):

$$\Delta T = 1.715 \times 10^6 \times \frac{-1.49 \times 10^{-6}}{21.97}; \quad \Delta T = -0.12 \text{ K.}$$

Therefore, the melting point of ice drops by 0.12 K

Part (B)

The spouse of an engineer showed scientific interest in asking:

- (i) What is the temperature in our pressure cooker?
- (ii) Why does it cook faster than in an ordinary saucepan?

Given: Pressure regulator weighs 78 g and sits on a 2.618 mm outer diameter opening; $\Delta H^\circ_{\text{vap}}$ for water at 1 atm and 100 °C is 40585 J mole⁻¹. What would your answers be for (i) and (ii) above?

Solution

For this problem, we have to calculate the pressure inside the cooker using Clausius–Clapeyron equation. To do so, we need to multiply the weight of the regulator by 9.8 to find the force that it exerts over the area defined by the gage opening:

$$P_{\text{cooker}} = \frac{F}{A} = \frac{78 \times 10^{-3} \times 9.8 \text{ [N]}}{0.25\pi \times (2.618 \times 10^{-3})^2 [\text{m}^2]} = 1.42 \times 10^5 \text{ Pa.}$$

With the cooker pressure, we can fix the following conditions: $P_1 = 1.01325 \times 10^5 \text{ Pa}$ (1 atm), $P_2 = 1.42 \times 10^5 \text{ Pa}$, $T_1 = 373 \text{ K}$ (100 °C), and $T_2 = \text{cooker temperature at the cooker pressure } P_2$. These values along with that of the heat of vaporization can be inserted now in Clausius–Clapeyron equation and solve for T_2 :

$$\begin{aligned} \ln\left(\frac{P_2}{P_1}\right) &= -\frac{\Delta H^\circ_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ \ln\left(\frac{1.42}{1.01325}\right) &= -\frac{40585}{8.314} \left(\frac{1}{T_2} - \frac{1}{373}\right) \\ &= -\frac{0.3375}{4881.53} = \frac{1}{T_2} - \frac{1}{373} \\ T_2 &= 383 \text{ K}; \quad T_2 = 110^\circ \text{C.} \end{aligned}$$

Thus answering to the engineer's spouse we have that (i) the cooker reaches 110 °C and (ii) since the pressure increases so does the boiling temperature, then meals are cooked faster.

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