

Geofluids — Part IV

Introduction to Geochemical and Reactive Transport Modeling

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1. Thermodynamic models of aqueous, gaseous, and mineral phases

Aqueous phase

Activity coefficient model for aqueous ionic species, Davies model

Activity coefficient model for $\text{H}_2\text{O}(\text{aq})$, Davies model

Activity coefficient model for $\text{CO}_2(\text{aq})$, Drummond model

Gaseous phase

Mineral phase

Thermodynamic models of aqueous, gaseous, and mineral phases

Activities – the effective concentrations of the species

- Let c_i denote concentration of species i (**Note:** sometime in literature it is denoted by $[i]$, but is different to species amount n_i).
- If we would use c_i instead of activities a_i to calculate the chemical potentials, then

$$\mu_i = \mu_i^o + RT \ln a_i \quad \text{can be reformulated by} \quad \mu_i = \mu_i^o + RT \ln(c_i/c_i^o)$$

where c_i^o is a reference concentration

- **But!** This simplification provides **accurate predictions only in some limited cases**:
 - gases at low pressures and high temperatures (close to ideal gas behavior)
 - very dilute electrolyte solutions (close to ideal solution behavior)

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Activities – corrected species “concentrations” in non-ideal mixtures

- Because of the **non-ideal behavior of the mixtures**, the concentrations of the species must be corrected:

$$a_i = \gamma_i(T, P, c) \frac{c_i}{c_0},$$

where γ_i is an **activity coefficient**, a function of (T, P, c) , with c denoting a **vector of concentrations of all species in the solution**.

- To calculate γ_i , there different (theoretical) **activity models**:
 - Davis equation,
 - Debye-Hückel equation,
 - Pitzer equations, etc.

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Thermodynamic models of aqueous, gaseous, and mineral phases

Aqueous phase

Activities of aqueous solute species

- The **activity of aqueous solute species**, such as $\text{H}^+(\text{aq})$, $\text{HCO}_3^-(\text{aq})$, $\text{CO}_2(\text{aq})$, is defined as:

$$a_i = \gamma_i m_i,$$

where:

- γ_i is the **activity coefficient** of solute species i ; and
- m_i is the **molality** of solute species i .

- The **molality** m_i of the i th aqueous species is form of describing concentrations and is defined as follows:

$$m_i = \frac{n_i}{\text{mass of solvent species } \text{H}_2\text{O}(\text{aq})},$$

or equivalently:

$$\begin{aligned} m_i &= \frac{n_i}{\text{molar mass}(\text{H}_2\text{O}(\text{aq})) \cdot n_{\text{H}_2\text{O}(\text{aq})}} \\ &= \frac{n_i}{18.01528 \cdot 10^{-3} \cdot n_{\text{H}_2\text{O}(\text{aq})}} \\ &= 55.508 \frac{n_i}{n_{\text{H}_2\text{O}(\text{aq})}}. \end{aligned}$$

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Molarity vs. molality

- The **molarity** c_i of the i th species is:

$$\begin{aligned}c_i &= \frac{n_i}{\text{volume of solvent species H}_2\text{O(aq)}} \\&= \frac{n_i \cdot \rho_{\text{H}_2\text{O(aq)}}}{\text{mass of solvent species H}_2\text{O(aq)}},\end{aligned}$$

where $\rho_{\text{H}_2\text{O(aq)}}$ is **water density** at given T and P .

- Measured in units of **molar** = mol/L (or mol/Lw or 10^3 mol/m^3).

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Ionic strength of aqueous solutions

- Most activity models for aqueous solutions depends on the **ionic strength**:

$$I = \frac{1}{2} \sum_{i=1}^{\text{solutes}} m_i Z_i^2,$$

where:

- m_i is the **molality** of species i ; and
 - Z_i is the **electric charge** of species i .
- I is a measure (in molal) of *how much concentrated is the solution with ionic species*,
- Note:** **Neutral species** play no role in I , just the ions.

- Question:** What is the ionic strength I of a solution obtained by mixing 1 kg of H₂O and:

- a) 2 mol of NaCl?
- b) 1 mol of CaCl₂?

<http://etc.ch/paWu> or



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- Answer:** a) 2 molal, b) 3 molal

Calculating species molalities and ionic strength, Exercise

Index	Species	Amount (mol)
1	H ₂ O(aq)	55.4551
2	H ⁺ (aq)	$1.23485 \cdot 10^{-4}$
3	OH ⁻ (aq)	$8.39739 \cdot 10^{-11}$
4	Na ⁺ (aq)	0.92
5	Cl ⁻ (aq)	0.92
6	CO ₃ ⁻² (aq)	$4.93648 \cdot 10^{-11}$
7	HCO ₃ ⁻ (aq)	$1.23484 \cdot 10^{-4}$
8	CO ₂ (aq)	0.032861
9	CO ₂ (g)	1.96702
10	H ₂ O(g)	0.0531732

Exercise:

- Calculate the mass M_w of solvent water H₂O(aq) (in kg). Use 18.0154 g/mol as an approximated molar mass of water.
- Calculate the molalities m_i of the aqueous solute species (in molal).
- Calculate the ionic strength I of aqueous solution (in molal).

Calculating species molalities and ionic strength using Python i

```
1 import numpy
2
3 # Create a list with names of aqueous species of interest
4 aqueous_species = ['H2O(aq)', 'H+', 'OH-', 'Na+', 'Cl-', 'CO3--', 'HCO3-', '
    CO2(aq)']
5
6 # The index of species H2O(aq) used in the calculation of molalities
7 iH2O = 0
8
9 # Create a list with the electrical charges of each species
10 Z = []
11
12 # Create a list with the amounts (in moles) of each species
13 n = []
14
15 # Transform the list n into a Numpy array for numerical calculations
16 n = numpy.array(n)
```

Calculating species molalities and ionic strength using Python ii

```
17
18 # Calculate the molalities of all species
19 m =
20
21 # Calculate the ionic strength of the aqueous solution
22 I =
23
24 # Print the calculated ionic strength
25 print('Ionic strength of solution is %f molal.' % I)
26
27 # Print the calculated molality of each species
28 for i in range(len(aqueous_species)):
29     print('Molality of %s is %f molal.' % (aqueous_species[i], m[i]))
```

Listing 1: Calculating species molalities and ionic strength using Python

Source code: [polybox](#).

Calculating species molalities and ionic strength using Python – Output

```
1 Ionic strength of solution is 0.921001 molal.  
2 Molality of H2O(aq) is 55.508000 molal.  
3 Molality of H+ is 0.000124 molal.  
4 Molality of OH- is 0.000000 molal.  
5 Molality of Na+ is 0.920878 molal.  
6 Molality of Cl- is 0.920878 molal.  
7 Molality of CO3-- is 0.000000 molal.  
8 Molality of HCO3- is 0.000124 molal.  
9 Molality of CO2(aq) is 0.032892 molal.
```

Listing 2: Calculating species molalities and ionic strength using Python – Output

Answer: To check the correctness of gaps in the code, use the [source code](#).

Activity coefficient of aqueous ionic species, Davies model

- The **Davies activity coefficient model** calculates γ_i using:

$$\log_{10} \gamma_i = -A_\gamma Z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right),$$

where A_γ is the **Debye–Hückel parameter** defined as

$$A_\gamma = 1.824928 \cdot 10^6 \rho_{\text{H}_2\text{O}}^{1/2} (\epsilon_{\text{H}_2\text{O}} T)^{-3/2},$$

where $\rho_{\text{H}_2\text{O}}$ and $\epsilon_{\text{H}_2\text{O}}$ are the **density** and **dielectric constant of pure water**.

- For 25 °C and 1 bar, $A_\gamma = 0.5095$.
- Limitations of the model:** It is accurate for I is in the range 0.1–0.7 molal, which is equivalent to 1 kg of water mixed with 5.8–40.9 grams of NaCl (0.5-4 teaspoons of table salt).

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Activity coefficient of aqueous ionic species, Davies model, Exercise

- **Quiz:** What is the activity coefficient of species Na^+ in an aqueous solution with ionic strength $I = 0.1$ molal using the *Davies activity coefficient model*:

$$\log_{10} \gamma_{\text{Na}^+} = -A_\gamma Z_{\text{Na}^+}^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right), \quad \text{where } A_\gamma = 0.5095?$$



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- **Answer:** 0.7814.

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<http://etc.ch/paWu> or

- **Answer:** 0.7814.
- **Note:** In an ideal solution, $\gamma_i = 1$ for all species.

Question: Based calculated γ_{Na^+} , is an *ideal solution assumption* reasonable one?

Activity coefficient as a function of I , Davies model

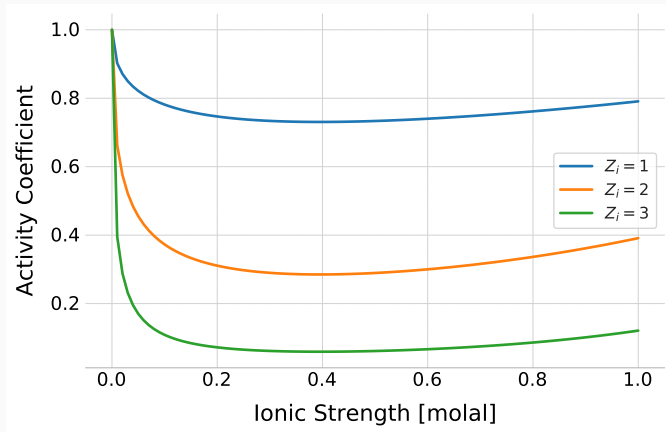


Figure 1: Activity coefficient γ_i for aqueous ions with charge $Z_i = 1, 2, 3$ as a function of I .

Question: How would these curves look like if the charges would be $Z_i = -1, -2, -3$?

Activity coefficient calculation in Python, Davies model i

```
1 import numpy
2 import matplotlib.pyplot as plt
3
4 # Function calculating activity coefficient according to the Davis model
5 def gamma_davies(Zi, I):
6     # Debye-Huckel parameter
7     Agamma = 0.5095
8     # Vector of ionic strength in the power 1/2
9     sqrtI = numpy.sqrt(I)
10    return 10**(-Agamma * Zi**2 * (sqrtI / (1.0 + sqrtI) - 0.3 * I))
11
12 # Create array with values of ionic strength in a range from 0.0 to 1.0
13 I = numpy.linspace(0.0, 1.0, 101)
14
15 # Calculate activity coefficients for different charges of the aqueous species
16 gammaZ1 = gamma_davies(1.0, I)
17 gammaZ2 = gamma_davies(2.0, I)
```

Activity coefficient calculation in Python, Davies model ii

```
18 gammaZ3 = gamma_davies(3.0, I)
19
20 # Plot an activity coefficient as a function of ionic strength for different
    charges
21 plt.xlabel('Ionic Strength [molal]')
22 plt.ylabel('Activity Coefficient')
23 plt.plot(I, gammaZ1, label=r'$Z_i=1$')
24 plt.plot(I, gammaZ2, label=r'$Z_i=2$')
25 plt.plot(I, gammaZ3, label=r'$Z_i=3$')
26
27 # Position the legend and save the figure
28 plt.legend(loc='center right')
29 plt.savefig('activity-coefficient-davies.pdf', bbox_inches='tight')
```

Listing 3: Davies activity model calculation in Python

Source code: *davies-activity-model.py*

Activity model for H₂O(aq), Davies model

- The **activity of H₂O(aq)** can be calculated using the following **Davies model**:

$$\ln a_{\text{H}_2\text{O(aq)}} = \frac{\ln 10}{55.5084} A_\gamma \left[2 \left(\frac{I + 2\sqrt{I}}{1 + \sqrt{I}} \right) - 4 \ln(1 + \sqrt{I}) - 0.3I^2 \right] - \frac{1 - x_{\text{H}_2\text{O(aq)}}}{x_{\text{H}_2\text{O(aq)}}},$$

where $x_{\text{H}_2\text{O(aq)}}$ is the mole fraction of H₂O(aq):

$$x_{\text{H}_2\text{O(aq)}} = \frac{n_{\text{H}_2\text{O(aq)}}}{\text{sum of moles of all aqueous species}}.$$

- Question:** Consider pure water as a solution. What is the value of ionic strength I and the activity of water $a_{\text{H}_2\text{O}}$?

<http://etc.ch/paWu> or



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Activity model for $\text{H}_2\text{O}(\text{aq})$, Davies model

- The **activity of $\text{H}_2\text{O}(\text{aq})$** can be calculated using the following **Davies model**:

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where $x_{\text{H}_2\text{O}(\text{aq})}$ is the mole fraction of $\text{H}_2\text{O}(\text{aq})$:

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- Question:** Consider pure water as a solution. What is the value of ionic strength I and the activity of water $a_{\text{H}_2\text{O}}$?

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- Answer:** $I = 0$, $a_{\text{H}_2\text{O}} = 1$.

Activity model for H₂O(aq), Ideal model

- For an **ideal solution**, all contribution arising from ionic strength can be eliminated:

$$\ln a_{\text{H}_2\text{O}(\text{aq})} = \frac{\ln 10}{55.5084} A_\gamma \left[2 \left(\frac{I + 2\sqrt{I}}{1 + \sqrt{I}} \right) - 4 \ln(1 + \sqrt{I}) - 0.3I^2 \right] - \frac{1 - x_{\text{H}_2\text{O}(\text{aq})}}{x_{\text{H}_2\text{O}(\text{aq})}} \quad (1)$$

$$= - \frac{1 - x_{\text{H}_2\text{O}(\text{aq})}}{x_{\text{H}_2\text{O}(\text{aq})}}. \quad (2)$$

- Let's investigate how accurate this approximation is?
- Source code: *activity-water-davies-vs-ideal.py*.

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Activity model for $\text{H}_2\text{O}(\text{aq})$: Davies vs. Ideal model

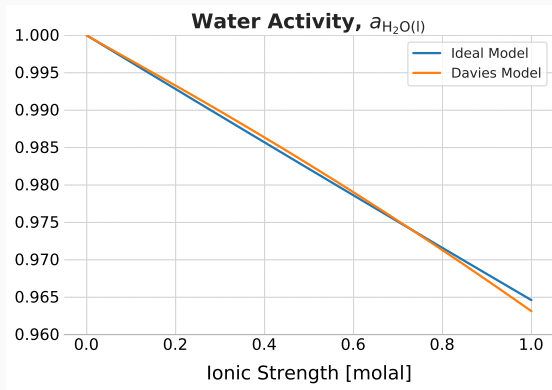


Figure 2: Activities of aqueous solvent species $\text{H}_2\text{O}(\text{aq})$ as a function of ionic strength I calculated using the Ideal and Davies models.

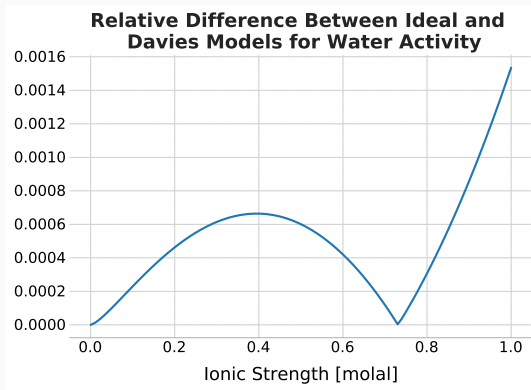


Figure 3: Relative difference between the Ideal and Davies models for activity of water as a function of ionic strength, I .

Activity coefficient model for $\text{CO}_2(\text{aq})$, Drummond model

- The **activity of the aqueous species $\text{CO}_2(\text{aq})$** can be calculated using

$$a_{\text{CO}_2(\text{aq})} = \gamma_{\text{CO}_2(\text{aq})} m_{\text{CO}_2(\text{aq})},$$

with $\gamma_{\text{CO}_2(\text{aq})}$ calculated using the **Drummond model**

$$\ln \gamma_{\text{CO}_2(\text{aq})} = \left(c_1 + c_2 T + \frac{c_3}{T} \right) I - (c_4 + c_5 T) \frac{I}{I + 1},$$

where T is temperature, I is the ionic strength of the aqueous solution, and $c_1 = -1.0312$, $c_2 = 1.2806 \cdot 10^{-3}$, $c_3 = 255.9$, $c_4 = 0.4445$ and $c_5 = -1.606 \cdot 10^{-3}$.

- Limitations of the model:** This equation is valid within the temperature and salinity ranges 20–400 °C and 0–6.5 molal, respectively.

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$$\ln \gamma_{\text{CO}_2(\text{aq})} = \left(c_1 + c_2 T + \frac{c_3}{T} \right) I - (c_4 + c_5 T) \frac{I}{I + 1},$$

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Calculating CO₂(aq) activity coefficient using Drummond model in Python i

```
1 # Import array and plotting libraries
2 import numpy
3 import matplotlib.pyplot as plt
4
5 # Function calculating activity of CO2(aq) according to the Drummond model
6 def gamma_drummond_co2(T, I):
7     c1, c2, c3, c4, c5 = -1.0312, 1.2806e-3, 255.9, 0.4445, -1.606e-3
8     return numpy.exp((c1 + c2*T + c3/T)*I - (c4 + c5*T)*I/(1 + I))
9
10 # Create an array with values of ionic strength in a range from 0.0 to 1.0
11 I = numpy.linspace(0.0, 1.0, 101)
12
13 # Define the temperatures for activity calculation
14 T1, T2, T3 = 50, 150, 250 # in celsius
15 # Calculate CO2(aq) activity for Drummond model for selected temperatures (in
    Kelvin)
16 gammaT1 = gamma_drummond_co2(T1 + 273.15, I)
```

Calculating $\text{CO}_2(\text{aq})$ activity coefficient using Drummond model in Python ii

```
17 gammaT2 = gamma_drummond_co2(T2 + 273.15, I)
18 gammaT3 = gamma_drummond_co2(T3 + 273.15, I)
19
20 # Plot CO2(aq) activity for Drummond model as a function an ionic strength for
    different T
21 plt.xlabel('Ionic Strength [molal]')
22 plt.ylabel('Activity Coefficient CO2(aq)')
23 plt.plot(I, gammaT1, label=r'T = %d$^\circ$C' % T1)
24 plt.plot(I, gammaT2, label=r'T = %d$^\circ$C' % T2)
25 plt.plot(I, gammaT3, label=r'T = %d$^\circ$C' % T3)
26 plt.legend(loc='best')
27 plt.savefig('activity-coefficient-co2-drummond.pdf', bbox_inches='tight')
```

Listing 4: Calculating $\text{CO}_2(\text{aq})$ activity coefficient in Python

Source code: *activity-coefficient-co2-drummond.py*.

Activity coefficient model for $\text{CO}_2(\text{aq})$, Drummond model

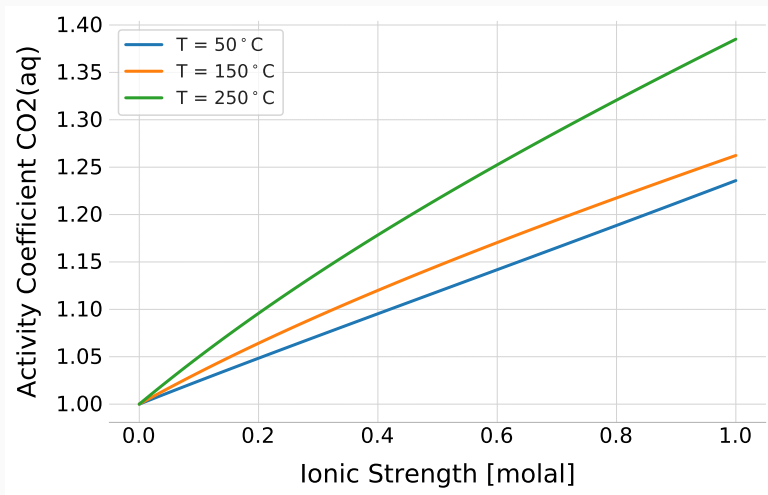
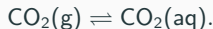


Figure 4: Activity coefficient of $\text{CO}_2(\text{aq})$ calculated using Drummond model at temperatures 50, 150, and 250 °C as a function of ionic strength.

Salting-out effect

- Consider the dissolution reaction for $\text{CO}_2(\text{g})$:



- At equilibrium, the following **mass action equation** is satisfied, i.e., $K(T, P) := \frac{a_{\text{CO}_2(\text{aq})}}{a_{\text{CO}_2(\text{g})}}$.
- Combining $a_{\text{CO}_2(\text{aq})} = K(T, P) a_{\text{CO}_2(\text{g})}$ and $a_{\text{CO}_2(\text{aq})} = \gamma_{\text{CO}_2(\text{aq})} m_{\text{CO}_2(\text{aq})}$, we obtain

$$m_{\text{CO}_2(\text{aq})} = \frac{1}{\gamma_{\text{CO}_2(\text{aq})}} K(T, P) a_{\text{CO}_2(\text{g})}(T, P) \approx \frac{1}{\gamma_{\text{CO}_2(\text{aq})}} f(T, P).$$

- Quiz:** What happens to $m_{\text{CO}_2(\text{aq})}$ when $\gamma_{\text{CO}_2(\text{aq})}$ increases with I for constant (T, P) ?

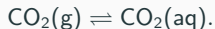


<http://etc.ch/paWu> or

- Answer:** $m_{\text{CO}_2(\text{aq})}$ decrease.

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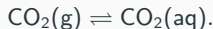


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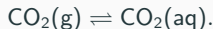


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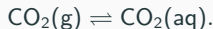
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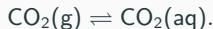
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Summary on the calculation of activities of aqueous species

- The **activities** of aqueous solute species

$$a_i = \gamma_i m_i.$$

- The **molality** of the species

$$m_i = 55.508 \frac{n_i}{n_{\text{H}_2\text{O(aq)}}}.$$

- The **ionic strength** of the aqueous solution

$$I = \frac{1}{2} \sum_i m_i Z_i^2.$$

- The **activity coefficient** γ_i for **ionic species** (e.g., Na^+ , Cl^- , HCO_3^- , etc.) according to the Davies model:

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Thermodynamic models of aqueous, gaseous, and mineral phases

Gaseous phase

Activities of species in a gaseous solution

- The **activity of gaseous species i** can be calculated using:

$$a_i = \varphi_i x_i \frac{P}{P^o},$$

where

- φ_i is the **fugacity coefficient** of the gaseous species,
 - x_i is the **mole fraction** of the gaseous species,
 - P is pressure (in units of bar, with $1 \text{ bar} = 10^5 \text{ Pa}$), and
 - P^o is a reference pressure, $P^o = 1 \text{ bar}$.
- The **fugacity coefficients of ideal gases** are $\varphi_i = 1$. **But:** the gases rarely behaving ideal.

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Activity of CO₂(g) using a cubic equation of state

- An **ideal gas** solution has a **PVT behavior** defined by the equation:

$$\frac{PV}{RT} = 1,$$

where P is pressure (in units of Pa), T is temperature (in units of K), V is molar volume (in units of m³/mol), and $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

- For **real gases**, we introduce a **compressibility factor** Z defined as

$$Z = \frac{PV}{RT} < 1.$$

- For **real gases**, $Z \rightarrow 1$ only when
 - temperatures are very high or
 - pressures are very low.

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Compressibility factor of gases i

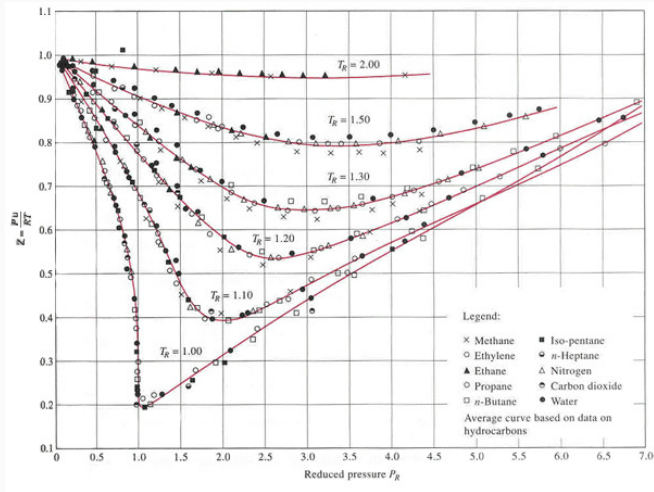


Figure 5: The compressibility factor Z as a function of reduced pressure $P_R = P/P_{\text{critical}}$ for several reduced temperatures $T_R = T/T_{\text{critical}}$ (Cengel and Boles, 2011).

Compressibility factor of gases ii

- Different gases have similar thermodynamic behavior when T and P are normalized by their critical values T_{critical} and P_{critical} , respectively.
- This allows us to use **single equation of state** to model the PVT behavior of a gas.

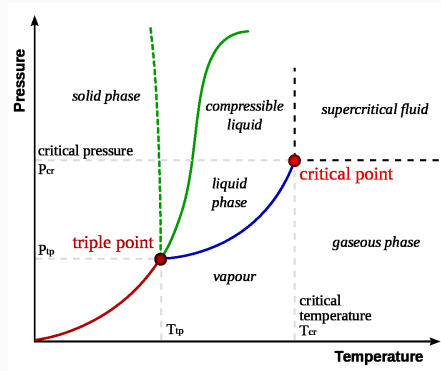


Figure 6: A typical phase diagram of a substance. The critical point is the limit point in the liquid-vapor saturation curve.

Supercritical carbon dioxide CO₂(g)

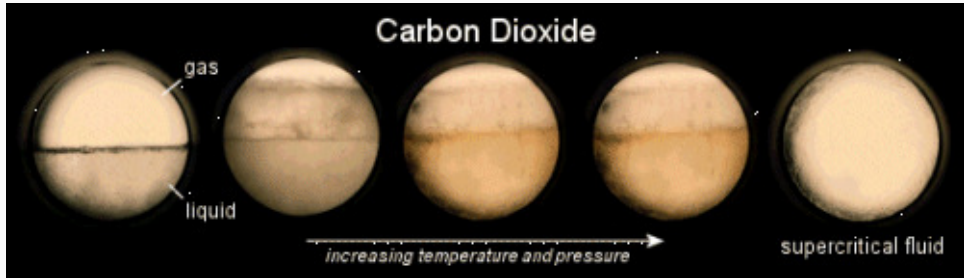


Figure 7: CO₂ initially existing in two phases: liquid and gas. As temperature and pressure increase, it transitions to a state in which there is only one phase in the **supercritical state**.

- As a **supercritical fluid**, the substance flows like a gas (less viscous than liquid) and is dense like a liquid.
- In geologic CO₂ sequestration, the supercritical state is more advantageous because of its **high mobility and high density**.

Cubic equation of state

- A **general cubic equation of state** can be written in terms of Z (Smith et al., 2005) as

$$1 = \frac{1}{Z - \beta} - q\beta \frac{1}{(Z + \epsilon\beta)(Z + \sigma\beta)},$$

where

- ϵ and σ are pure numbers (same for all substances),
- β and q are parameters specific to substances and defined as

$$\beta = \Omega \frac{P_r}{T_r} \quad \text{and} \quad q = \frac{\Psi}{\Omega} \frac{\alpha(T_r, \omega)}{T_r}$$

with specific to a **particular equation of state** Ω , Ψ , and $\alpha(T)$,

- the **reduced temperature and pressure** $T_r = \frac{T}{T_c}$ and $P_r = \frac{P}{P_c}$ are defined via **critical temperature and pressure** T_c and P_c , and
- ω is a **acentric factor** that depends on the substance.

- **Note:** For $\text{CO}_2(\text{g})$, $T_c = 304.2 \text{ K}$, $P_c = 73.83 \text{ bar}$, $\omega = 0.224$.

Cubic equation of state, Different models i

Equation of State	ϵ	σ	Ω	Ψ
Ideal Gas	0	0	0	0
van der Waals (vdW) ¹ (1873)	0	0	1/8	27/64
Redlich/Kwong (RK) ² (1949)	0	1	0.08664	0.42748
Soave/Redlich/Kwong (SRK) ³ (1972)	0	1	0.08664	0.42748
Peng/Robinson (PR) ⁴ (1976)	$1 - \sqrt{2}$	$1 + \sqrt{2}$	0.07780	0.45724

¹van der Waals (1873); ²Redlich & Kwong (1949); ³Soave (1972), commonly known as Soave–Redlich–Kwong;

⁴Peng & Robinson (1976).

Table 1: The parameters ϵ , σ , Ω , and Ψ for different equation of states.

Activity of CO₂(g) using a cubic equation of state iii

Equation of State	$\alpha(T_r, \omega)$
Ideal Gas	0
van der Waals (vdW) ¹ (1873)	1
Redlich/Kwong (RK) ² (1949)	$T_r^{-1/2}$
Soave/Redlich/Kwong (SRK) ³ (1972)	$\left[1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})\right]^2$
Peng/Robinson (PR) ⁴ (1976)	$\left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{1/2})\right]^2$

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Table 2: The function $\alpha(T_r, \omega)$ for different equations of state.

PV phase diagram with isotherms

- The area in **green** is a region in which **liquid and vapour coexist**.
- There are three **isotherms**: **subcritical**, **critical**, and **supercritical**.
- The horizontal **blue segment** corresponds to the fluid change from liquid to vapour at a constant T and P .

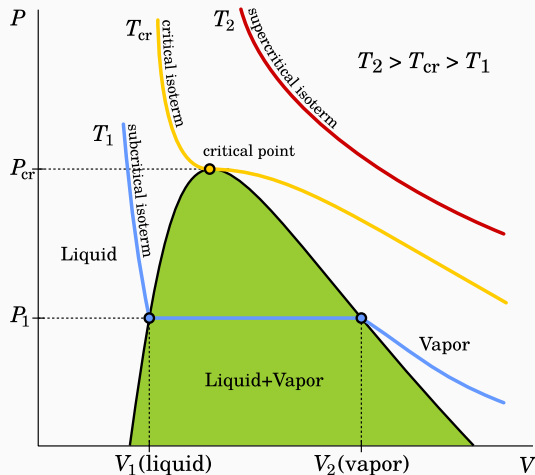


Figure 8: Illustration of a PV phase diagram of a substance.

PV phase diagram with isotherms, Roots of cubic EOS i

- Because we are modeling the PVT behavior of a substance using a **cubic equation of state**:

$$Z^3 + AZ^2 + BZ + C = 0,$$

where $Z = \frac{PV}{RT}$ is compressibility factor, “spurious” behavior can happen as shown on the next figure.

- This equation of state has **utmost three roots**.

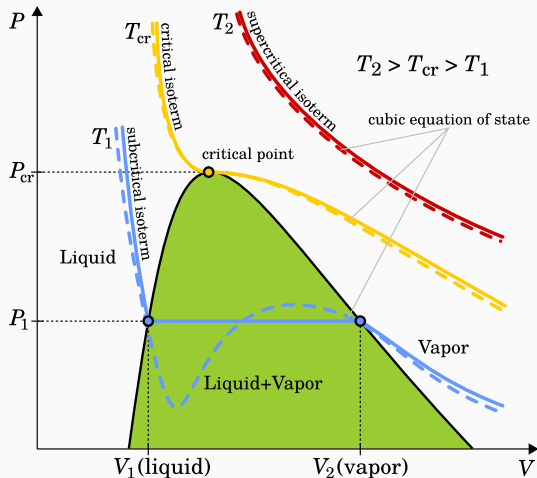


Figure 9: Illustration of a PV phase diagram of a substance.

PV phase diagram with isotherms, Roots of cubic EOS ii

- When three real roots exists for cubic equation of state
 - the **smallest real value** possibly corresponds to the **liquid state** and
 - the **largest real value** possibly corresponds to the **gaseous state**.
- Any root inside the green region is a **mathematical artefact** of the cubic model.
- **Quiz:** Which value of Z are we interested in for $\text{CO}_2(\text{g})$?



<http://etc.ch/paWu> or

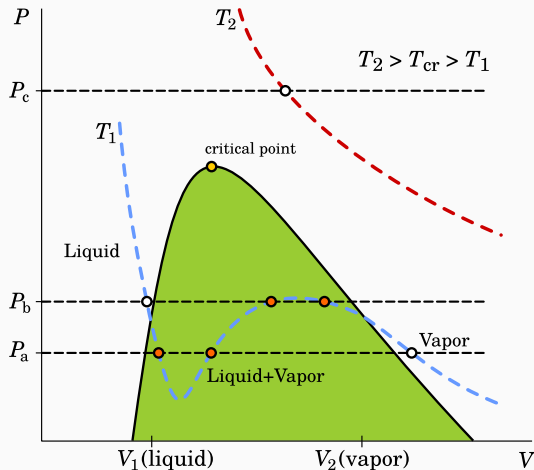


Figure 10: Illustration of a PV phase diagram of a substance with roots of cubic equation of state.

PV phase diagram with isotherms, Roots of cubic EOS ii

- When three real roots exists for cubic equation of state
 - the **smallest real value** possibly corresponds to the **liquid state** and
 - the **largest real value** possibly corresponds to the **gaseous state**.
- Any root inside the green region is a **mathematical artefact** of the cubic model.
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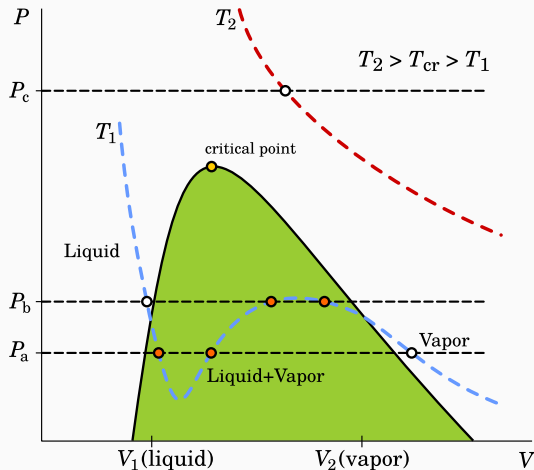


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PV phase diagram with isotherms, Roots of cubic EOS ii

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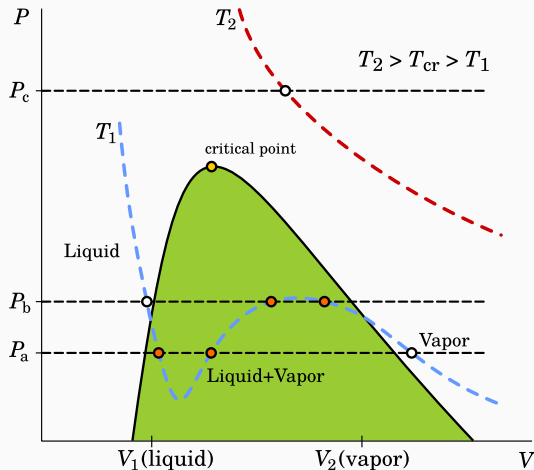


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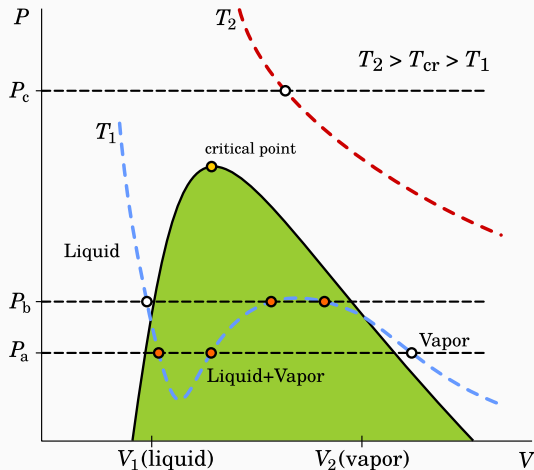


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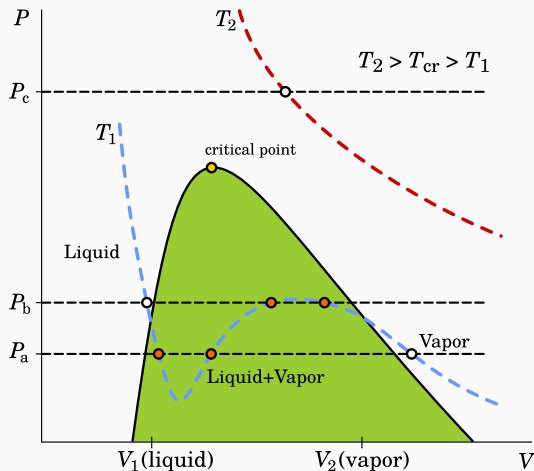


Figure 10: Illustration of a PV phase diagram of a substance with roots of cubic equation of state.

PV phase diagram with isotherms, Roots of cubic EOS ii

- When three real roots exist for cubic equation of state
 - the **smallest real value** possibly corresponds to the **liquid state** and
 - the **largest real value** possibly corresponds to the **gaseous state**.
- Any root inside the green region is a **mathematical artefact** of the cubic model.
- Quiz:** Which value of Z are we interested in for $\text{CO}_2(\text{g})$?

<http://etc.ch/paWu> or



Answer: as we are interested in vapor ($\text{CO}_2(\text{g})$) properties, we need **the largest root of cubic EOS**.

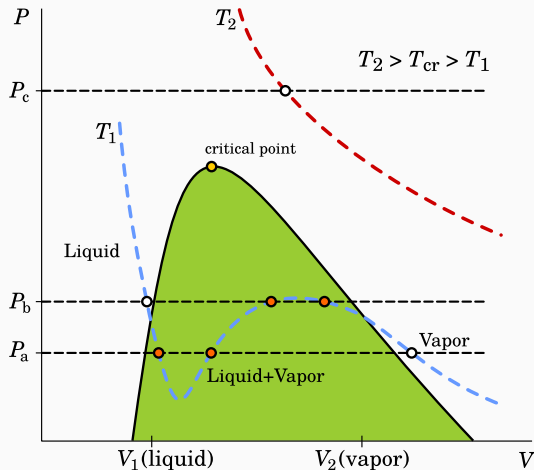


Figure 10: Illustration of a PV phase diagram of a substance with roots of cubic equation of state.

Calculating the compressibility factor of CO₂, Fixed point iteration

- The equation of state is non-linear in Z , so that its solution requires an **iterative procedure**.
- We rearrange it to a more convenient form for **the largest root** computation (Smith et al., 2005)

$$Z = f(Z) = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

and apply simplest iterative approach, the so-called **fixed-point iteration method**:

- the **initial guess**

$$Z^0 = 1,$$

- the i^{th} **iteration**

$$Z^{i+1} = f(Z^i) = 1 + \beta - q\beta \frac{Z^i - \beta}{(Z^i + \epsilon\beta)(Z^i + \sigma\beta)},$$

- the **acceptance criterion** $|Z^{i+1} - Z^i| < \epsilon$, where ϵ is selected tolerance.

Calculating the compressibility factor of CO₂, Fixed point iteration

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- the **acceptance criterion** $|Z^{i+1} - Z^i| < \epsilon$, where ϵ is selected tolerance.

Calculating the compressibility factor of CO₂, Python code i

```
1 from numpy import *
2 import matplotlib.pyplot as plt
3
4 # Function that calculates the fixed point of equation  $x = f(x)$ 
5 def fixed_point(f, x0):
6     """
7     :param f: the function
8     :param x0: the initial guess for the fixed point
9     :return x: the fixed point of the equation  $x = f(x)$ 
10    """
11
12    # Tolerance and max number of iterations
13    maxiters = 100
14    tolerance = 1e-4
15
16    # Counter for the number of iterations
17    counter = 0
```

Calculating the compressibility factor of CO₂, Python code ii

```
18
19     # Initial guess
20     x = x0
21
22     # Perform one or more fixed point iterations
23     for counter in range(maxiters):
24
25         # Calculate the new approximation for x
26         x_new = f(x)
27
28         # Check the new value for convergence
29         if abs(x_new - x) < tolerance:
30             return x # return x if the calculation converged
31
32         # Update x with x_new
33         x = x_new
34
```

Calculating the compressibility factor of CO₂, Python code iii

```
35     # Raise an error if the calculation did not converge.
36     raise RuntimeError('Could not calculate the \
37         solution of the nonlinear equation in %d iterations.' % counter)
38
39 # Function to calculate Z using fixed point method
40 def compressibility_factor_fixedpoint(T, P, omega, Tc, Pc):
41     """
42     :param T: temperature
43     :param P: pressure
44     :param omega: the acentric factor
45     :param Tc: critical temperature
46     :param Pc: critical pressure
47     :return Z: compressibility factor
48     """
49
50     # Parameters of Peng-Robinson EOS
51     epsilon = 1 - sqrt(2.0)
```

Calculating the compressibility factor of CO₂, Python code iv

```
52     sigma = 1 + sqrt(2.0)
53     Omega = 0.07780
54     Psi = 0.45724
55
56     # Reduced temperature and pressure
57     Tr = T / Tc
58     Pr = P / Pc
59
60     # Evaluation of the alpha(Tr, omega) function
61     alpha = (1 + (0.37464 + 1.54226 * omega - 0.26992 * omega**2) * (1 - sqrt(
62         Tr))))**2
63
64     # Constants beta and q
65     beta = Omega * Pr/Tr
66     q = Psi/Omega * alpha/Tr
67
68     # Initial guess for Z
```

Calculating the compressibility factor of CO₂, Python code v

```
68     Z0 = 1.0
69
70     # Define the function f that represents the nonlinear equation  $x = f(x)$ 
71     def f(Z):
72         return (1 + beta - q*beta*(Z - beta)/((Z + epsilon*beta)*(Z + sigma*
73         beta)))
74
75     return fixed_point(f, Z0) # use fixed point function to perform the
76     calculation of Z
77
78 # The array with temperature values in K
79 temperatures = linspace(60.0, 300.0, 9) + 273.15
80
81 # The array with pressure values in bar
82 pressures = linspace(1.0, 400.0, 101)
83
84 # The critical temperature and pressure of CO2
```


Calculating the compressibility factor of CO₂, Python code vi

```
83 TcC02 = 304.2
84 PcC02 = 73.83
85
86 # The acentric factor of C02
87 omegaC02 = 0.224
88
89 # Create a plot
90 plt.xlabel('Pressure [bar]')
91 plt.ylabel(r'$Z = \frac{PV}{RT}$')
92 plt.ylim(0.05, 1.05)
93 plt.title('Compressibility Factor of C02(g)\nUsing Fixed Point Method')
94
95 # Plot one curve for each temperature in array temperatures
96 for T in reversed(temperatures):
97     # Create a list with Z values at current T and P from the array pressures
98     Z = [compressibility_factor_fixedpoint(T, P, omegaC02, TcC02, PcC02) for P
          in pressures]
```

Calculating the compressibility factor of CO₂, Python code vii

```
99     # Plot the values of Z over all pressure points and current temperature T
100     plt.plot(pressures, Z, label=r'$T=%.0f\;^{\circ}\mathrm{C}$' % (T -
101         273.15))
102     # Position the legend and save the figure
103     plt.legend(loc='center left', bbox_to_anchor=(1, 0.5))
104     plt.savefig('co2-compressibility-factor-fixed-point.pdf', bbox_inches='tight')
```

Listing 5: Calculating the compressibility factor of CO₂ using fixed point method in Python

Source code: *co2-compressibility-factor-fixed-point.py*.

Calculating the compressibility factor of CO₂, Fixed point iteration i

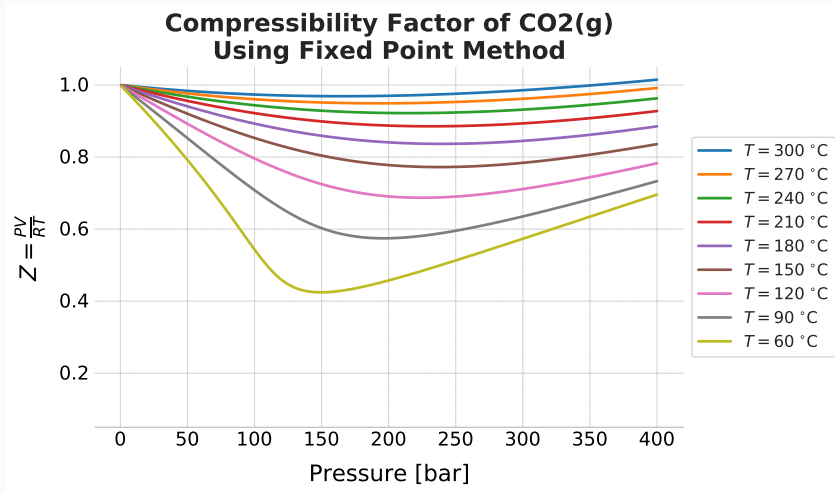


Figure 11: The compressibility factor Z of CO₂ for temperatures 60–300 °C and 1–400 bar calculated using fixed point iteration method.

Calculating the compressibility factor of CO₂, Fixed point iteration ii

- **Disadvantages** of the fixed point method:
 - **slow**, requiring many iterations; and
 - **unstable**, failing to converge.
- The fixed point method **failed at regions close to the liquid-vapor saturation curve**, for temperatures below $T_{cr} = 31.04$ °C and pressures close to the saturation pressure (i.e., near the blue curve).
- This is due to discontinuity of derivative in the function of Z at $T = T_{cr}$, whereas fixed point requires its **continuity**.
- **Solution:** Newton's method.

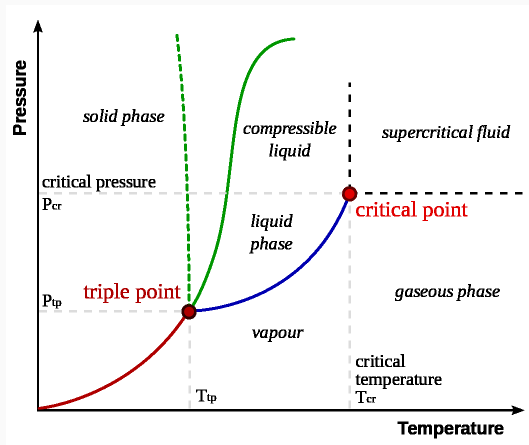


Figure 12: The phase diagram of a substance.

Calculating the compressibility factor of CO₂, Fixed point iteration ii

- **Disadvantages** of the fixed point method:
 - **slow**, requiring many iterations; and
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- This is due to discontinuity of derivative in the function of Z at $T = T_{cr}$, whereas fixed point requires its **continuity**.
- **Solution:** Newton's method.

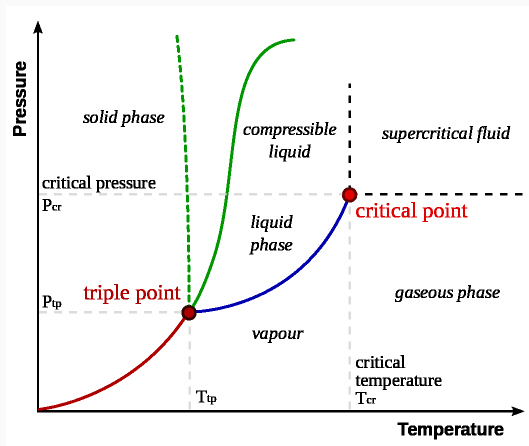


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Calculating the compressibility factor of CO₂, Fixed point iteration ii

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- This is due to discontinuity of derivative in the function of Z at $T = T_{cr}$, whereas fixed point requires its **continuity**.
- **Solution:** Newton's method.

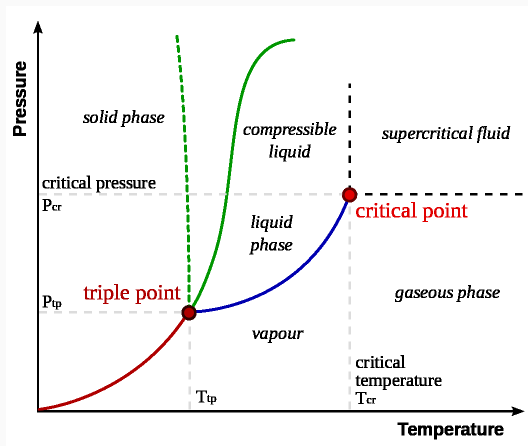


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Calculating the compressibility factor of CO₂, Fixed point iteration ii

- **Disadvantages** of the fixed point method:
 - **slow**, requiring many iterations; and
 - **unstable**, failing to converge.
- The fixed point method **failed at regions close to the liquid-vapor saturation curve**, for temperatures below $T_{cr} = 31.04$ °C and pressures close to the saturation pressure (i.e., near the blue curve).
- This is due to discontinuity of derivative in the function of Z at $T = T_{cr}$, whereas fixed point requires its **continuity**.
- **Solution:** Newton's method.

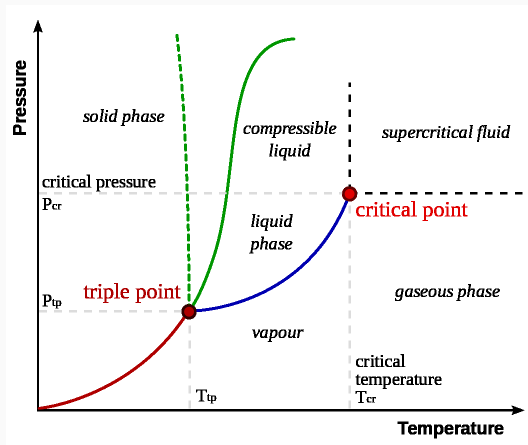


Figure 12: The phase diagram of a substance.

Compressibility factor of CO₂, Newton vs. Fixed point method

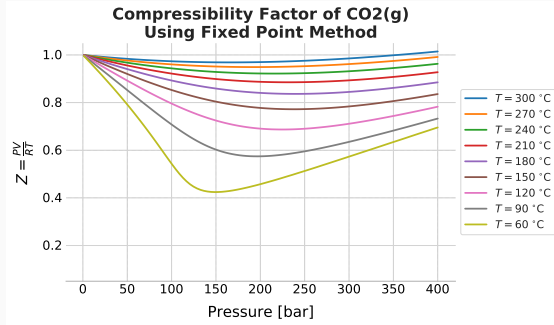


Figure 13: The compressibility factor Z of CO₂ for temperatures 60–300 °C and 1–400 bar using **fixed point iteration method**. **Failed computations for temperatures 0 and 30 °C!**

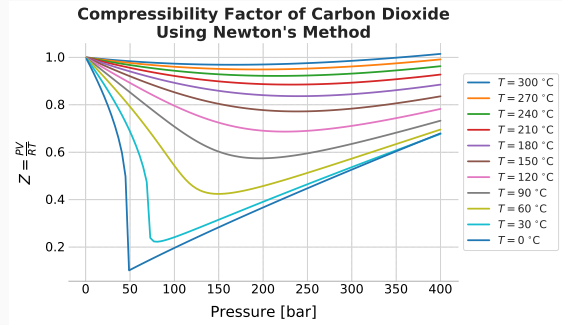


Figure 14: The compressibility factor Z of CO₂ for temperatures 0–300 °C and 1–400 bar using **Newton's method**. **Newton's method had no trouble for temperatures 0 and 30 °C!**

Calculating the compressibility factor of CO₂, Newton's method

- In **Newton's method**, we transform the non-linear equation $Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)}$ into the form $r(Z) = 0$, where r is the **residual function**

$$r(Z) = f(Z) - Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} - Z.$$

- Newton's method requires **first order derivative** of $r(Z)$ in its iterative process:
 - the **initial guess**

$$Z^0 = 1,$$

- i^{th} **iteration**

$$Z^{i+1} = Z^i - r(Z^i)/r'(Z^i),$$

where

$$r'(Z) = -\frac{q\beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \left\{ 1 - (Z - \beta) \frac{2Z + (\epsilon + \sigma)\beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \right\} - 1,$$

- and **acceptance criterion** $|r(Z^{i+1})| < \varepsilon$, where ε is selected tolerance.

Calculating the compressibility factor of CO₂, Python code i

```
1 from numpy import *
2 import matplotlib.pyplot as plt
3
4 # Function that solves the nonlinear equation  $r(x) = 0$ 
5 def newton(r, rprime, x0):
6     """
7     :param r: the function
8     :param rprime: the first derivative of f
9     :param x0: the initial guess for the root
10    :return x: the root of the equation  $f(x) = 0$ 
11    """
12
13    # Tolerance and max number of iterations
14    maxiters = 100
15    tolerance = 1e-4
16
17    # Counter for the number of iterations
```

Calculating the compressibility factor of CO₂, Python code ii

```
18     counter = 0
19
20     # Initial guess
21     x = x0
22
23     # Perform one or more Newton iterations
24     for counter in range(maxiters):
25
26         # Calculate the new approximation for x
27         x = x - r(x) / rprime(x)
28
29         # Check the new value for convergence
30         if abs(r(x)) < tolerance:
31             return x # return x if the calculation converged
32
33     # Raise an error if the calculation did not converge.
34     raise RuntimeError('Could not calculate the \
```

Calculating the compressibility factor of CO₂, Python code iii

```
35         solution of the nonlinear equation in %d iterations.' % counter)
36
37 # Function to calculate Z using Newton's method
38 def compressibility_factor_newton(T, P, omega, Tc, Pc):
39     """
40     :param T: temperature
41     :param P: pressure
42     :param omega: the acentric factor
43     :param Tc: critical temperature
44     :param Pc: critical pressure
45     :return Z: compressibility factor
46     """
47
48     # Parameters of Peng-Robinson EOS
49     epsilon = 1 - sqrt(2.0)
50     sigma = 1 + sqrt(2.0)
51     Omega = 0.07780
```

Calculating the compressibility factor of CO₂, Python code iv

```
52 Psi = 0.45724
53
54 # Reduced temperature and pressure
55 Tr = T / Tc
56 Pr = P / Pc
57
58 # Evaluation of the alpha(Tr, omega) function
59 alpha = (1 + (0.37464 + 1.54226*omega - 0.26992*omega**2)*(1 - sqrt(Tr)))
60 **2
61
62 # Constants beta and q
63 beta = Omega * Pr / Tr
64 q = Psi/Omega * alpha/Tr
65
66 # Residual function r that represents the nonlinear equation r(x) = 0
67 def r(Z):
```

Calculating the compressibility factor of CO₂, Python code v

```
67         return (1 + beta - q*beta*(Z - beta)/((Z + epsilon*beta)*(Z + sigma*
68         beta))) - Z
69
70     # First order derivative of function r'(x)
71     def rprime(Z):
72         aux = (Z + epsilon*beta)*(Z + sigma*beta)
73         return -q*beta/aux * (1.0 - (Z - beta)*(2*Z + (epsilon + sigma)*beta)/
74         aux) - 1
75
76     # Initial guess for Z
77     Z0 = 1.0
78
79     return newton(r, rprime, Z0) # use newton function to perform the
80     calculation of Z
81
82 # The array with temperature values in K
83 temperatures = linspace(0.0, 300.0, 11) + 273.15
```

Calculating the compressibility factor of CO₂, Python code vi

```
81
82 # The array with pressure values in bar
83 pressures = linspace(1.0, 400.0, 101)
84
85 # The critical temperature and pressure of CO2
86 TcCO2 = 304.2
87 PcCO2 = 73.83
88
89 # The acentric factor of CO2
90 omegaCO2 = 0.224
91
92 # Create a plot
93 plt.xlabel('Pressure [bar]')
94 plt.ylabel(r'$Z = \frac{PV}{RT}$')
95 plt.title('Compressibility Factor of Carbon Dioxide\nUsing Newton\'s Method')
96
97 # Plot one curve for each temperature in array temperatures
```

Calculating the compressibility factor of CO₂, Python code vii

```
98 for T in reversed(temperatures):
99     # Create a list with Z values at current T and P from the array pressures
100     Z = [compressibility_factor_newton(T, P, omegaCO2, TcCO2, PcCO2) for P in
           pressures]
101     # Plot the values of Z over all pressure points and current temperature T
102     plt.plot(pressures, Z, label=r'$T=%.0f\;^{\circ}\mathrm{C}$' % (T -
           273.15))
103
104 # Position the legend and save the figure
105 plt.legend(loc='center left', bbox_to_anchor=(1, 0.5))
106 plt.savefig('co2-compressibility-factor-newton.pdf', bbox_inches='tight')
```

Listing 6: Calculating the compressibility factor of CO₂ using Newton's method in Python

Source code: [polybox](#).

Calculating the compressibility factor of CO₂, Newton's method

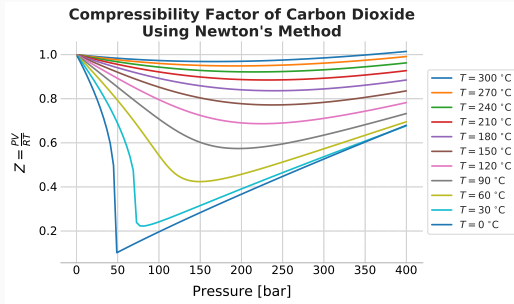


Figure 15: For $T < T_{\text{cr}}(\text{CO}_2) = 31.04\text{ }^{\circ}\text{C}$, the increase in pressure results in a phase transition from vapor to liquid.

Quiz: To which part of the phase diagram does the blue lines correspond to, if we are increasing P_1 to P_2 ?

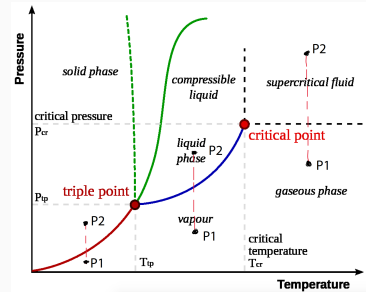


Figure 16: The phase diagram of a substance. $T_{\text{cr}}(\text{CO}_2) = 31.04\text{ }^{\circ}\text{C}$.



Calculating the compressibility factor of CO₂, Newton's method

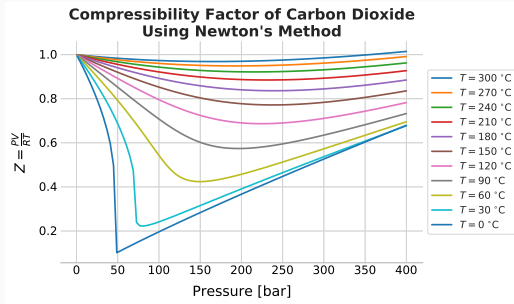


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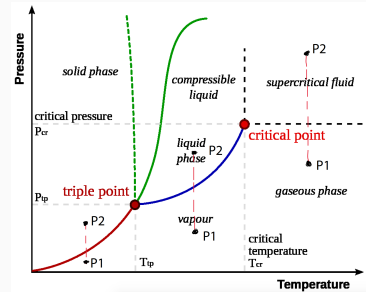


Figure 16: The phase diagram of a substance. $T_{\text{cr}}(\text{CO}_2) = 31.04\text{ }^{\circ}\text{C}$.



Calculating the compressibility factor of CO₂, Newton's method

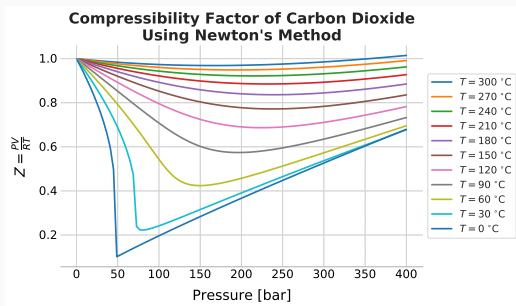


Figure 15: For $T < T_{cr}(\text{CO}_2) = 31.04\text{ }^{\circ}\text{C}$, the increase in pressure results in a phase transition from vapor to liquid.

Quiz: To which part of the phase diagram does the blue lines correspond to, if we are increasing P_1 to P_2 ?

Answer: to the middle.

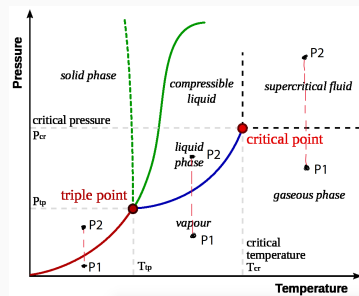


Figure 16: The phase diagram of a substance. $T_{cr}(\text{CO}_2) = 31.04\text{ }^{\circ}\text{C}$.



Activity of CO₂(g) using a cubic equation of state

- Once Z is calculated, the **fugacity coefficient of the gas** is computed using:

$$\ln \varphi_i := Z - 1 - \ln(Z - \beta) - q\theta,$$

where θ is defined as:

$$\theta := \begin{cases} \frac{1}{\sigma - \epsilon} \ln \left(\frac{Z + \sigma\beta}{Z + \epsilon\beta} \right) & \epsilon \neq \sigma \\ \frac{\beta}{Z + \epsilon\beta} & \epsilon = \sigma \end{cases}$$

dependent on the equation of state.

- The **activity of CO₂(g)** is calculated using:

$$a_{\text{CO}_2(\text{g})} = \varphi_{\text{CO}_2(\text{g})} \frac{P}{P^o},$$

with P measured in bar and $P^o = 1$ bar.

Fugacity coefficient of CO₂ following the calculation of Z

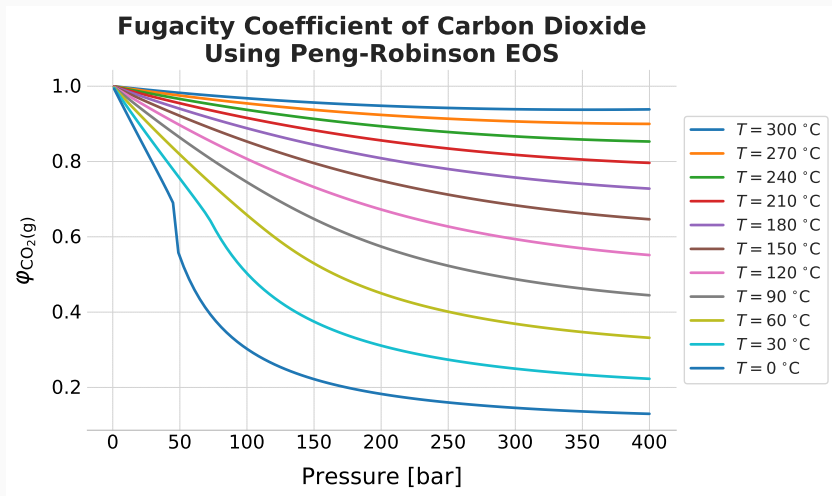


Figure 17: The fugacity coefficient of CO₂ using Peng–Robinson equation of state (EOS) for temperatures 0–300 °C and 1–400 bar.

Summary on the calculation of activities of gaseous species

- The **activities of gaseous species**:

$$a_i = \frac{\varphi_i x_i P}{P^o}.$$

- The **fugacity coefficient** of the $\text{CO}_2(\text{g})$:

$$\ln \varphi_i = Z - 1 - \ln(Z - \beta) - q\theta$$

- The **compressibility factor**

$$Z = \frac{PV}{RT} < 1$$

with $Z \equiv 1$ **only** when the substance is an **ideal gas**.

- Calculation of Z requires the solution of the **cubic equation of state**

$$Z = \frac{Z}{Z - \beta} - q\beta \frac{Z}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

by *fixed point method* or *Newton's method*.

Summary on the calculation of activities of gaseous species

- The **activities of gaseous species**:

$$a_i = \frac{\varphi_i x_i P}{P^o}.$$

- The **fugacity coefficient** of the $\text{CO}_2(\text{g})$:

$$\ln \varphi_i = Z - 1 - \ln(Z - \beta) - q\theta$$

- The **compressibility factor**

$$Z = \frac{PV}{RT} < 1$$

with $Z \equiv 1$ **only** when the substance is an **ideal gas**.

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$$Z = \frac{Z}{Z - \beta} - q\beta \frac{Z}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

by *fixed point method* or *Newton's method*.

Summary on the calculation of activities of gaseous species

- The **activities of gaseous species**:

$$a_i = \frac{\varphi_i x_i P}{P^o}.$$

- The **fugacity coefficient** of the $\text{CO}_2(\text{g})$:

$$\ln \varphi_i = Z - 1 - \ln(Z - \beta) - q\theta$$

- The **compressibility factor**

$$Z = \frac{PV}{RT} < 1$$

with $Z \equiv 1$ **only** when the substance is an **ideal gas**.

- Calculation of Z requires the solution of the **cubic equation of state**

$$Z = \frac{Z}{Z - \beta} - q\beta \frac{Z}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

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Thermodynamic models of aqueous, gaseous, and mineral phases

Mineral phase

Summary on the calculation of activities of mineral species

- The activities of pure minerals (e.g., mineral phases composed by a single mineral only) is:

$$a_i = 1.$$

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