

Section 2

Equations of State

Now that we have reviewed our understanding of thermodynamics and the tools we can use to analyse our systems, we now require a surrogate model to mimic these systems. These models are referred to as equations of state. These equations are simply functions, f , which take in our conditions (\mathbf{x}) and give us a thermodynamic property, Y :

$$Y = f(\mathbf{x})$$

Typically, these functions are written in terms of the system volume, V , temperature, T , and composition, N_i , and give us either the pressure, p , or Helmholtz free energy, A :

$$p = f(V, T, \mathbf{N})$$

$$A = f(V, T, \mathbf{N})$$

There are numerous equations of state available, each with their own benefits. It is the objective of this section to give you a high-level understanding of the equations of state, details of their implementation and guidance on how to go about selecting one for a particular application.

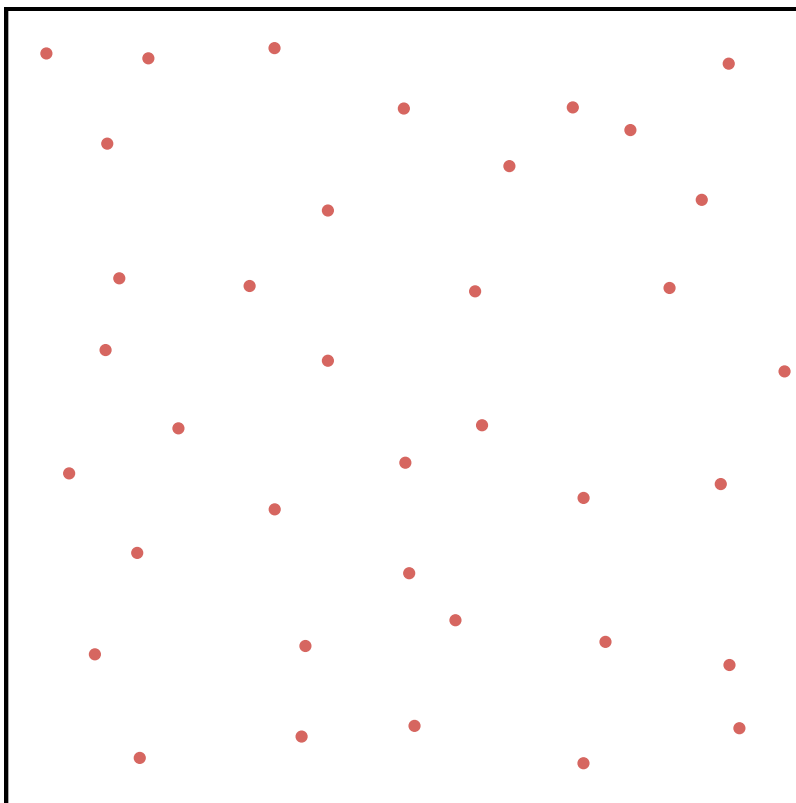
Section 2.1

Ideal gas

As a common starting ground, let us examine an equation of state most of us will have encountered during our time in highschool: the Ideal gas equation, initially formulated by Emille Clapeyron. Typically, it is written as:

$$pV = Nk_B T$$

where k_B is the Boltzmann constant and N is the total number of particles. The ideal gas equation models species as infinitesimally small particles with perfectly elastic collisions. Visually:



One might think that, because of its simple nature, the ideal gas is not suitable for most practical applications. However, not only do simple spherical species (such as noble gases and methane) agree well with it, even typically complex species, such as water, eventually begin to behave ideally. This is, of course, limited to the gas phase at low pressures. For certain applications, this may be sufficient.

However, in expressing the ideal gas equation in terms of the pressure, we are not considering the full picture of an ideal gas. Let us consider the Helmholtz free energy, which can be obtained by integrating the pressure in terms of the volume:

$$A = - \int p dV = -Nk_{\text{B}}T \int \frac{1}{V} dV = -Nk_{\text{B}}T \ln V + c(N, T)$$

Indeed, as shown above, there is an additional constant present in the above expression which could depend on the composition and temperature of our system. If derived from statistical mechanics, one will find that this constant is related to the rotational and vibrational contributions present within a molecule. In most engineering applications, to account for these contributions, rather than use the complex expression obtained from statistical mechanics, ideal isobaric heat capacity correlations are typically used. A standard functional form for these correlations is a simple cubic:

$$C_p = a + bT + cT^2 + dT^3$$

From here, we can use our first laws of thermodynamics to obtain the ideal Helmholtz free energy from the ideal isobaric heat capacity:

$$dA = dH - TdS - Vdp$$

Remembering that:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

One should then be able to obtain an expression for A in terms of integrals of C_p :

$$\frac{A}{Nk_B T} = \ln \frac{V_0}{V} + \frac{1}{Nk_B T} \int_{T_0}^T C_p dT + \frac{H_0}{Nk_B T} - \frac{1}{Nk_B} \int_{T_0}^T \frac{C_p}{T} dT - \ln \frac{T}{T_0} - \frac{S_0}{Nk_B} - 1$$

where H_0 and S_0 are the enthalpy and entropy of formation, typically neglected as these do not contribute for most properties of interest. V_0 and T_0 are the conditions of the reference states which are also typically neglected. One simple test to make sure our expression for the ideal term is correct is to verify the high-temperature limit for the molar ideal isobaric heat capacity where, for linear molecules, we expect:

$$C_{p,\text{lim}} = \frac{7}{2}R + (3N_{\text{atoms}} - 5)R$$

and, for non-linear molecules:

$$C_{p,\text{lim}} = 4R + (3N_{\text{atoms}} - 6)R$$

For example, let us consider the ideal gas model for methane (whose limit should be **13R**):

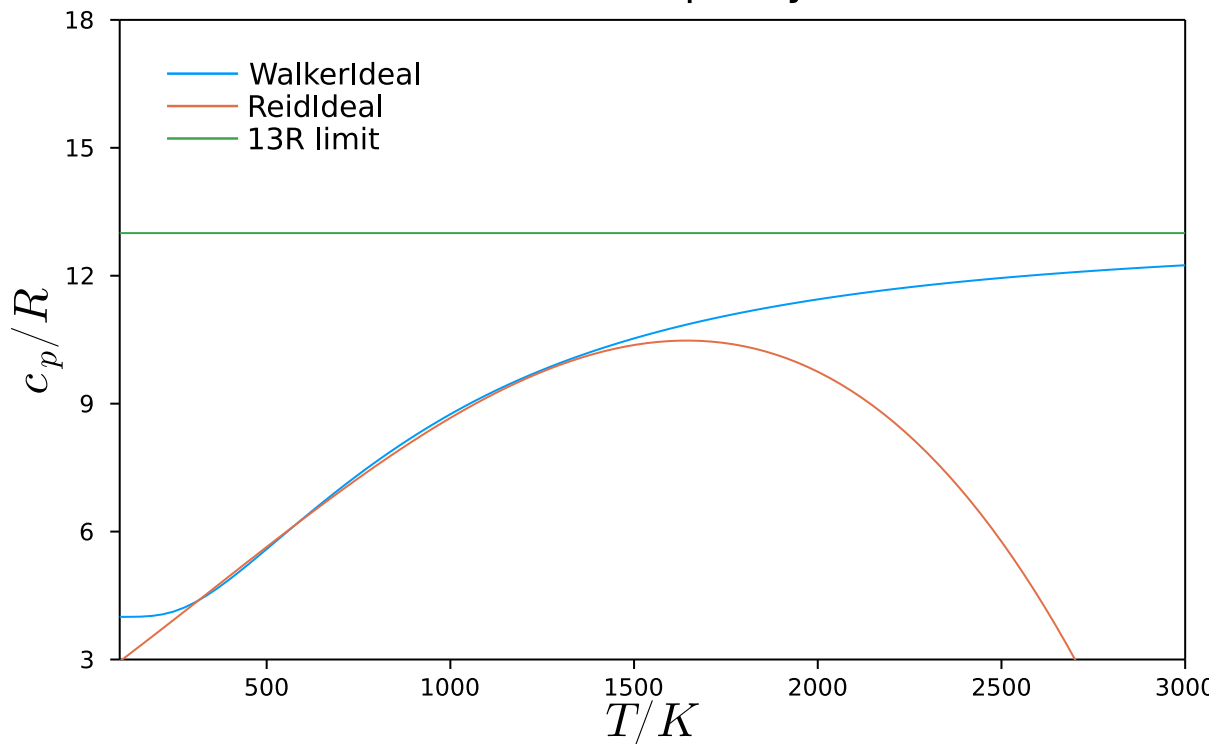
[24.5687, 26.1623, 27.769, 29.3871, 31.0149, 32.6506, 34.2925, 35.939, 37.5884, 39.2389, 41.0000]

```

• begin
•   model1 = WalkerIdeal(["methane"])
•   model2 = ReidIdeal(["methane"])
•
•   T = range(100,3000,length=100)
•
•   Cp1 = isobaric_heat_capacity.(model1,1e5,T)
•   Cp2 = isobaric_heat_capacity.(model2,1e5,T);
•
• end

```

Ideal isobaric heat capacity of methane

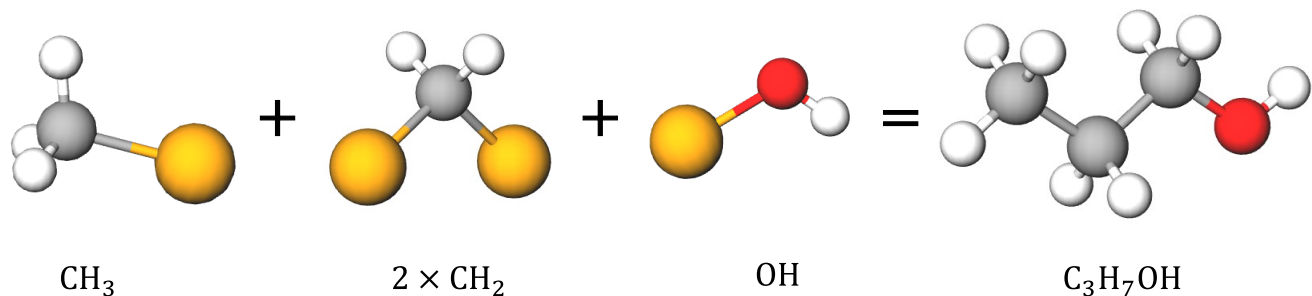


In the above, we use the theoretically-rigorous approach by Walker and Haslam (WalkerIdeal), which always ensures the high and low temperature limits are met, and the empirical Reid polynomial (ReidIdeal). As we can see, without considering experimental data, the ReidIdeal model doesn't satisfy the high (and low) temperature limits, meaning we should only use this model around intermediate temperature (300 K-1000 K) which is where most of our systems should be anyways.

In terms of ideal gas models, there are many to choose from but generally fall into two categories: 1. Species-specific and 2. Group contribution. As previously mentioned, Reid polynomials, a species-specific equation, obtain the molar ideal heat capacity as:

$$c_p = a + bT + cT^2 + dT^3$$

where the parameters *a*, *b*, *c* and *d* are all species-specific. This generally means that the values obtained for the ideal heat capacity should be quite accurate. However, if we start dealing with unconventional species, where species-specific parameters are not available, then we will have to resort to a group contribution method. In a group-contribution method, species are split into fragments (known as groups) which can be re-assembled to make new species. An example is shown below:



Typically, the groups and their occurrence (or multiplicity) can be specified within a group-contribution based model:

```
model =
JobackIdeal with 1 component:
"propanol": "-CH3" => 1, "-CH2-" => 2, "-OH (alcohol)" => 1
Contains parameters: Mw, N_a, T_c, P_c, V_c, T_b, T_m, H_form, G_form, a, b, c, d, H_fusioi
• model = JobackIdeal([("propanol",["-CH3"=>1,"-CH2-"=>2,"-OH (alcohol)"=>1])])
```

Each of these groups has a set of parameters assigned to it. As an example, let us consider the Joback method which correlates multiple properties, as well as the ideal heat capacity. Here, the ideal heat capacity of a species can be obtained as:

$$C_p = \sum_k n_k(a_k - 37.93) + T \sum_k n_k(b_k - 0.210) + T^2 \sum_k n_k(c_k - 3.91 \times 10^{-4}) + T^3 \sum_k n_k(d_k - 1.15 \times 10^{-6})$$

where a_k , b_k , c_k and d_k are all group-specific parameters and n_k is the occurrence of a group k in a particular species.

Whilst this method is quite simple, one of the failings of group contribution is, given we are now trying to fit a larger dataset with fewer parameters, the accuracy will inevitably be reduced, in comparison to species-specific correlations. However, the accuracy of the method can generally be improved based on how the groups are selected; if a group covers a larger set of atoms, we can expect that it will provide a better estimate of the ideal heat capacity. For example, when modelling ethanol, using CH₃ and CH₂OH groups instead of CH₃, CH₂, and OH groups would most likely result in more accurate estimates of the heat capacity. This argument holds true for any group contribution methodology.

Note: with the advent of machine learning, many ideal heat capacity correlations that leverage these tools have also been developed. However, as these can only really be treated as a black box, for the purposes of this course, we have chosen to omit these.

As a general rule, if a species-specific approach is available for your system of interest, implementation aside, the values obtained can be trusted. When using a group contribution approach, it is recommended to spend some time verifying that the values obtained are realistic (for example, does the high-temperature limit match what we would expect if we count up the number of rotations and vibrations?).

Commonly-used species-specific ideal gas models:

- Reid polynomials: A 3rd order polynomial
- NASA polynomials: A 5th order polynomial
- Wilhoit correlation: A piecewise function which contains multiple non-polynomial terms
- Aly and Lee: A physically-based approach but with fewer parameters than the above

Group-contribution ideal gas models:

- Joback method: A 3rd order polynomial
- Coniglio *et al.*: A more-physically based approach with second-order groups.
- Walker and Haslam: A physically based approach with special treatment of halogens

To get a better understanding of the importance of the ideal term on real properties, below we consider an example where the advanced equation of state, PC-SAFT, provides the residual properties, with and without the appropriate ideal term, for a species and pressure of your choice:

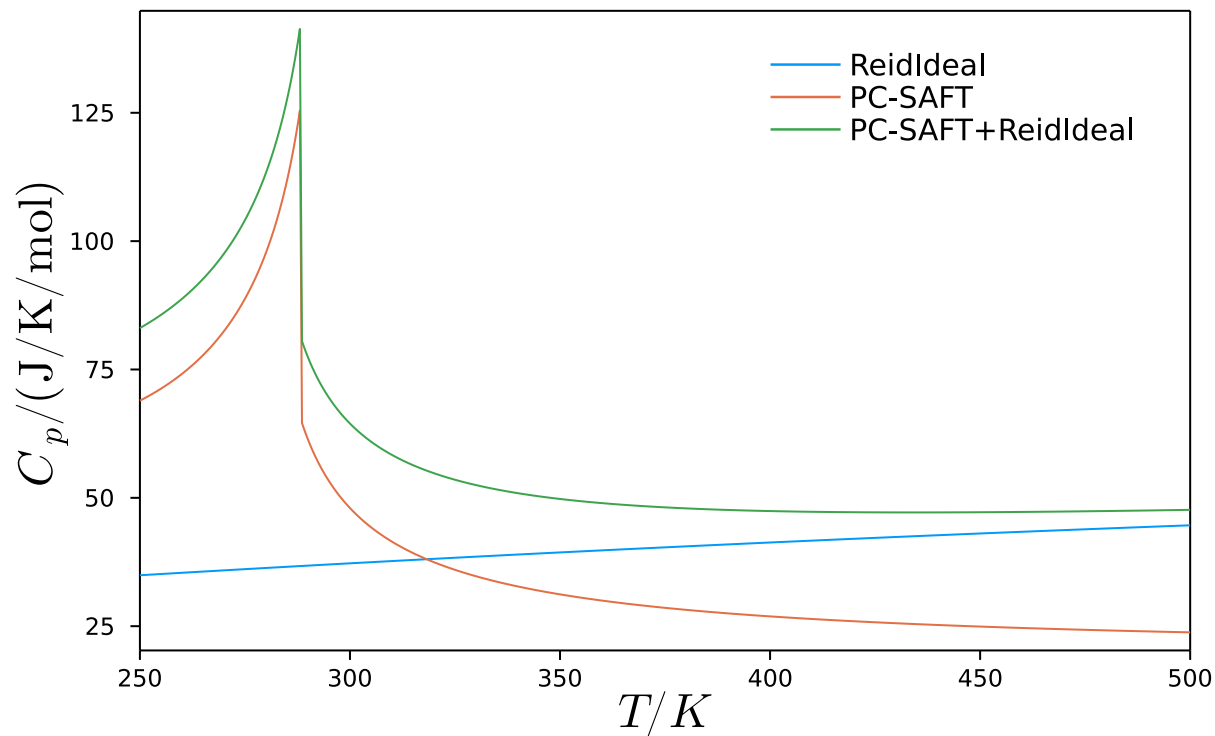
5.0e6

```

• begin
•   species = "carbon dioxide"
•   p = 5e6;
• end

```

Isobaric heat capacity with different EoS at $p = 10$ MP



As we can see, the ideal model represents a non-negligible contribution to our overall property where, at high temperatures, it practically becomes the only contribution which matters (even with species like water).

Nevertheless, once the best ideal model has been selected, all that is needed is to then integrate it using the equation for the Helmholtz free energy given earlier. Leveraging automatic differentiation will then make it possible to obtain all other properties.

