

## 11.2: Behaviors of Non-Ideal Gases

Non-ideal gases (sometimes also referred to as “real gases”), do not behave as ideal gases because at least one of the assumptions in [Definition: Ideal Gas](#) is violated. What characterizes non-ideal gases is that there is no unique equation that we can use to describe their behavior. For this reason, we have a plethora of several experimental models, none of which is superior to the other. The van der Waals (vdW) equation is the only model that we will analyze in detail because of its simple interpretation. However, it is far from universal, and for several non-ideal gases, it is severely inaccurate. Other popular non-ideal gases equations are the Clausius equation, the virial equation, the Redlich–Kwong equation and several others.<sup>1</sup>

### The van der Waals equation

One of the simplest empirical equation that describes non-ideal gases was obtained in 1873 by Johannes Diderik van der Waals (1837–1923). The vdW equation includes two empirical parameters ( $a$  and  $b$ ) with different values for different non-ideal gases. Each of the parameters corresponds to a correction for the breaking of one of the two conditions that define the ideal gas behavior ([Definition: Ideal Gas](#)). The vdW equation is obtained from the ideal gas equation performing the following simple substitutions:

$$P \rightarrow \left( P + \frac{a}{\bar{V}^2} \right)$$

$$\bar{V} \rightarrow (\bar{V} - b),$$

which results in:

$$P\bar{V} = RT \rightarrow \left( P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}.$$

The parameter  $a$  accounts for the presence of intermolecular interactions, while the parameter  $b$  accounts for the non-negligible volume of the gas molecules. Despite the parameters having simple interpretations, their values for each gas must be determined experimentally. Values for these parameters for some significant non-ideal gas are reported below:

	$a \left[ \frac{\text{L}^2 \text{bar}}{\text{mol}^2} \right]$	$b \left[ \frac{\text{L}}{\text{mol}} \right]$
Ammonia	4.225	0.0371
Argon	1.355	0.03201
Carbon dioxide	3.640	0.04267
Carbon monoxide	1.505	0.03985
Chlorine	6.579	0.05622
Freon	10.78	0.0998
Helium	0.0346	0.0238
Hydrogen	0.2476	0.02661
Mercury	8.200	0.01696
Methane	2.283	0.04278
Neon	0.2135	0.01709
Nitrogen	1.370	0.0387

	$a \left[ \frac{\text{L}^2 \text{bar}}{\text{mol}^2} \right]$	$b \left[ \frac{\text{L}}{\text{mol}} \right]$
Oxygen	1.382	0.03186
Radon	6.601	0.06239
Xenon	4.250	0.05105

## Joule–Thomson effect

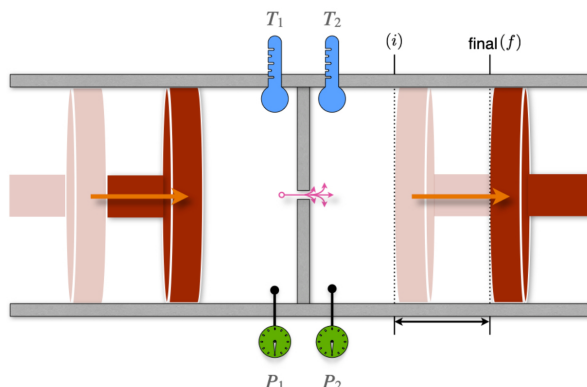


Figure 11.2.1: The Joule–Thomson Experiment.

We have already met William Thomson, also known as Lord Kelvin, and his seminal work on the second law of thermodynamics. In conjunction with that work, Thomson is famous for developing a sensitive method for measuring the temperature changes related to the expansion of a gas. These experiments improved on the earlier work by James Joule, and Lord Kelvin's improved instrument depicted in Figure 11.2.4 is named the Joule–Thomson apparatus. The apparatus is composed of two chambers, each with its own mobile piston. The chambers are connected via a valve or a porous plug. The entire equipment is also thermally isolated from the surroundings. This instrument is a more sensitive version of the Joule expansion apparatus that we already described in [section 3](#) (compare with [Figure 3.1.1](#)).

Thomson realized that a gas flowing through an obstruction experience a drop in pressure. If the entire apparatus is insulated, it will not exchange heat with its surroundings ( $Q = 0$ ), and each transformation will happen at adiabatic conditions. Let's consider an initial condition with 1 mol of gas in the left chamber, occupying a volume  $V_l$ , and a completely closed right chamber, for which  $V_r^i = 0$ . After the process completes, the volume of the right chamber will reduce to  $V_l^f = 0$ , while the volume of the right chamber will be  $V_r$ . Using the first law of thermodynamics, we can write:

$$\Delta U = U_r - U_l = \underbrace{Q}_{=0} + W = W_l + W_r, \quad (11.2.1)$$

with:

$$W_l = - \int_{V_l}^0 P_l dV = P_l V_l$$

$$W_r = - \int_0^{V_r} P_r dV = -P_r V_r.$$

Replacing [???](#) into Equation [11.2.1](#), results in:

$$\begin{aligned} U_r - U_l &= P_l V_l - P_r V_r \\ \underbrace{U_r + P_r V_r}_{H_r} &= \underbrace{U_l + P_l V_l}_{H_l}, \end{aligned}$$

which, replacing the definition of enthalpy  $H = U + PV$ , we obtain:

$$H_r = H_l$$

$$\Delta H = 0,$$

or, in other words, the process is **isenthalpic**. Using the total differential of  $H$ :

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP = C_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP, \quad (11.2.2)$$

we obtain:

$$\Delta H = \int dH = \int C_P dT + \int \left( \frac{\partial H}{\partial P} \right)_T dP = 0, \quad (11.2.3)$$

or, in purely differential form:

$$dH = C_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP = 0, \quad (11.2.4)$$

From Equation 11.2.4 we can define a new coefficient, called the *Joule–Thomson coefficient*,  $\mu_{JT}$ , that measures the rate of change of temperature of a gas with respect to pressure in the Joule–Thomson process:

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_P} \left( \frac{\partial H}{\partial T} \right)_P \quad (11.2.5)$$

The value of  $\mu_{JT}$  depends on the type of gas, the temperature and pressure before expansion, and the heat capacity at constant pressure of the gas. The temperature at which  $\mu_{JT}$  changes sign is called the “Joule–Thomson inversion temperature.” Since the pressure decreases during an expansion,  $\partial P$  is negative by definition, and the following possibilities are available for  $\mu_{JT}$ :

Gas temperature:	$\partial P$	$\mu_{JT}$	$\partial T$	The gas will:
<i>Below the inversion temperature</i>	–	+	–	cool
<i>Above the inversion temperature</i>	–	–	+	warm

For example, helium has a very low Joule–Thomson inversion temperature at standard pressure ( $T = 4.5 \text{ K}$ ), and it warms when expanded at constant enthalpy at typical room temperatures. The only other gases that have standard inversion temperature lower than room temperature are hydrogen and neon. On the other hand, nitrogen and oxygen have high inversion temperatures ( $T = 621 \text{ K}$  and  $T = 764 \text{ K}$ , respectively), and they both cool when expanded at room temperature. Therefore, it is possible to use the Joule–Thomson effect in refrigeration processes such as air conditioning.<sup>2</sup> As we already discussed in [chapter 3](#), the temperature of an ideal gases stays constant in an adiabatic expansion, therefore its Joule–Thomson coefficient is always equal to zero.

1. For more information on empirical equations for non-ideal gases see [this Wikipedia page](#).
2. Nitrogen and oxygen are the two most abundant gases in the air. A sequence of Joule–Thomson expansions are also used for the industrial liquefaction of air.

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