

## 10.1: Introduction

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Equation 8.4.3,  $TV^{-1} = \text{constant}$ , tells us how to calculate the drop in temperature if a gas expands adiabatically and reversibly; it is expanding against an external pressure (e.g., a piston), and, in pushing the piston back, the molecules are doing external work and are losing kinetic energy. What happens, however, if a gas expands into a vacuum? Suppose that the gas is held inside a cylinder not by a metal piston but by a thin membrane, and the membrane breaks, so that the molecules rush out into empty space. This is obviously an *irreversible* expansion; it is most unlikely that all of the molecules will ever find their way back to the cylinder. The molecules are doing no external work. If the gas is an ideal gas, there are no intermolecular forces, so the gas does no internal work. There is nothing to slow down the molecules in their headlong escape from the cylinder. The temperature will remain unaltered by the expansion. On the other hand, if the gas is not an ideal gas, there will be van der Waals attractive forces between the molecules, so the molecules will slow down slightly when the gas expands and there will be a small drop in temperature. But we also recall, from the van der Waals model, that at close intermolecular distances, the forces between the molecules are predominantly repulsive Coulomb forces, so it is also possible that, if the gas starts out very dense and it expands irreversibly as we have described, it may initially become slightly warmer as the repulsive Coulomb forces push the molecules apart and speed them on their way.

The Joule and Joule-Thomson experiments are concerned with these scenari.

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