

## 10.13: The second-dependence of the Energy and Enthalpy of A Real Gas

Let us consider the effects that intermolecular forces of attraction and repulsion must have in the adiabatic free expansion ( $P_{\text{applied}} = 0$ ) of a real gas. In such an expansion, no energy can be exchanged between the gas and its surroundings.

Suppose that the molecules of the gas are attracted to one another. Then energy must be expended to separate the molecules as the expansion takes place. (To achieve the expansion, work must be done against the intermolecular attractive forces.) Since the system cannot obtain this energy from its surroundings, it must be obtained by decreasing the translational kinetic energy (and the rotational and vibrational energy) of the gas molecules themselves. This means that the temperature of the gas must decrease during the expansion.

Conversely, if the molecules repel one another, energy is released as the expansion takes place, and the temperature of the gas increases during the expansion. The temperature can remain unchanged after the adiabatic free expansion only if the effects of the intermolecular forces of attraction and repulsion offset one another exactly.

We can express these conclusions more precisely by saying that we expect  $(\partial T / \partial P)_E > 0$  if forces of attraction dominate the intermolecular interactions. We expect  $(\partial T / \partial P)_E < 0$  if forces of repulsion dominate. Now, as a matter of mathematics, we have

$$\left(\frac{\partial E}{\partial P}\right)_T = -\left(\frac{\partial E}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_E$$

As a matter of experience, increasing the temperature of any gas at constant pressure always increases the energy of the gas; that is, we observe  $(\partial E / \partial T)_P > 0$ . It follows that we can expect

$$\left(\frac{\partial E}{\partial P}\right)_T < 0$$

(attraction dominates)

when intermolecular forces of attraction dominate and

$$\left(\frac{\partial E}{\partial P}\right)_T > 0$$

(repulsion dominates)

when forces of repulsion dominate.

In the Joule experiment, a gas is allowed to expand into an initially evacuated container. The Joule experiment is a direct test of these ideas; however, as we have noted, it is difficult to carry out accurately. Fortunately, a simple modification of the Joule experiment produces an experiment that is much more sensitive. Instead of allowing the gas to expand freely into a fixed volume, we allow it to expand adiabatically against a constant applied pressure. This is the Joule-Thomson experiment. In the next section, we show that the enthalpy of the gas does not change in such a process. We measure the temperature change as the gas expands adiabatically from an initial, constant, higher pressure to a final, constant, lower pressure. Since this process occurs at constant enthalpy, the Joule-Thomson experiment measures

$$\left(\frac{\partial T}{\partial P}\right)_H$$

from which we can obtain

$$\left(\frac{\partial H}{\partial P}\right)_T$$

To interpret the Joule-Thomson experiment in terms of intermolecular forces, we need to show that

$$\left(\frac{\partial H}{\partial P}\right)_T < 0$$

(attraction dominates)

at pressures and temperatures where intermolecular forces of attraction dominate and

$$\left(\frac{\partial H}{\partial P}\right)_T > 0$$

(repulsion dominates)

where forces of repulsion dominate. To do this using an explicit mathematical model for a real gas, let us find

$$\left(\frac{\partial E}{\partial P}\right)_T$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T$$

for a van der Waals gas. Writing van der Waals equation in terms of the molar volume,  $(P + a/\bar{V}^2)(\bar{V} - b) = RT$ , and introducing

$$\gamma(P, \bar{V}) = P - \frac{a}{\bar{V}^2} + \frac{2ab}{\bar{V}^3}$$

so that we can express the results more compactly, we find

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{\gamma(P, \bar{V})}{\bar{V} + b}$$

so that

$$\left(\frac{\partial \bar{V}}{\partial P}\right)_T = -\frac{\bar{V} + b}{\gamma(P, \bar{V})}$$

and

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{\gamma(P, \bar{V})}$$

Substituting into results we develop in [Section 10.5](#), we have

$$\left(\frac{\partial \bar{E}}{\partial P}\right)_T = -P\left(\frac{\partial \bar{V}}{\partial P}\right)_T - T\left(\frac{\partial \bar{V}}{\partial T}\right)_P = -\frac{a(\bar{V} - b)}{\bar{V}^2 \gamma(P, \bar{V})}$$

and

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \bar{V} + T\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \bar{V} + \frac{RT}{\gamma(P, \bar{V})}$$

We introduce van der Waals equation in [Section 2.12](#). By the argument we make there, the  $(P + a/\bar{V}^2)$  term models the effects of attractive intermolecular interactions when  $a > 0$ . By a parallel argument, we can see that it models the effects of repulsive interactions when  $a < 0$ . Parameter  $b$  models the effects of intermolecular repulsive interactions that come into play when the molecules come into contact with one another. For present purposes, we can consider molecules for which  $b = 0$ ; this simplifies our equations without affecting the description they give of the phenomena that are of current interest.

This gives us a model in which the effects of intermolecular interactions are described by the values of a single parameter that has a straightforward physical interpretation. Thus, we can write

$$(P + a/\bar{V}^2)\bar{V} = RT$$

to describe a gas of point-mass molecules that experience intermolecular forces. When  $a > 0$ , these forces are attractive; when  $a < 0$  they are repulsive. (For any given real gas, our equation can only be an approximation that is valid over a limited range of conditions. In some ranges,  $a > 0$ ; in others,  $a < 0$ .) With  $b = 0$  we must have

$$\gamma(P, \bar{V}) = P - \frac{a}{\bar{V}^2} > 0$$

(If  $\gamma(P, \bar{V}) \leq 0$ , we have  $(\partial P / \partial \bar{V})_T \geq 0$ . As a matter of experience, the pressure of a gas always decreases with increasing volume at constant temperature. It follows that van der Waals equation with  $b = 0$  and  $(P - a/\bar{V}^2) \leq 0$  cannot describe any gas.) With  $b = 0$  we have

$$\left( \frac{\partial \bar{E}}{\partial P} \right)_T = \frac{-a}{\bar{V} (P - a/\bar{V}^2)}$$

and

$$\left( \frac{\partial \bar{H}}{\partial P} \right)_T = RT \left[ \frac{1}{P + a/\bar{V}^2} - \frac{1}{P - a/\bar{V}^2} \right]$$

For a gas at conditions in which forces of attraction dominate, we have  $a > 0$ , so that

$$\left( \partial \bar{E} / \partial P \right)_T < 0 \text{ and } \left( \partial \bar{H} / \partial P \right)_T < 0$$

(attraction dominates)

Conversely, at conditions in which forces of repulsion dominate, we have  $a < 0$ , and

$$\left( \partial \bar{E} / \partial P \right)_T > 0 \text{ and } \left( \partial \bar{H} / \partial P \right)_T > 0$$

(repulsion dominates)

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