

## Joule-Thomson Expansion

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### 1. Introduction

We are at the point where we can make our first analysis of an actual experiment.<sup>1</sup> The experiment will be explained first. Then thermodynamics will be used to show that the experiment is *isoenthalpic* (meaning a constant enthalpy process). With this result, we can then explain the main result of the experiment in terms of the properties of the gases involved.

### 2. The Joule-Thomson Experiment

The apparatus itself is quite simple. Imagine a tube with a porous plate separating it into two parts. The porous plate will allow a gas to go through it, but only slowly. It acts as a *throttle*. On each side of the plate there is a piston that fits the tube tightly. Each piston can (in principle) be pushed up against the porous plate. The tube itself is insulated so that no heat can enter or leave the tube.<sup>2</sup>

The experiment is also quite simple. Imagine that some gas is placed between the porous plate and the piston on the left side of the tube. This is side 1. On the other side the piston is flush against the porous plate. This is side 2.

The initial volume of gas on side 1 is  $V_1$ . The pressure is  $p_1$  and the temperature  $T_1$ .

Now during the experiment gas is pushed through the porous plate by pushing on the piston on the left side. At the same time the piston on the right side is pulled in such a way that the pressure on the right side is always  $p_2$ .<sup>3</sup>

At the end of the experiment all of the gas has been pushed through the porous plate. The volume on side 1 is zero. The final volume on the right side (side 2) is  $V_2$ , the pressure is  $p_2$  and the temperature  $T_2$ .

The curious result of this experiment is that careful measurement shows that  $T_2$  is *not* equal to  $T_1$ . Under some conditions it is higher, under others it is lower.

The problem is to decide how to analyse this.

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<sup>1</sup> Although we do need to drag in one result that will not be obtained until later in the course.

<sup>2</sup> There is a drawing of the apparatus on page 69 of Atkins.

<sup>3</sup> Of course,  $p_2$  must be *less* than  $p_1$ .

### 3. Initial Analysis

The process starts with volume  $V_1 = V_1$  and volume  $V_2 = 0$ . It ends with volume  $V_1 = 0$  and volume  $V_2 = V_2$ . The work done on the left side is:  $w_1 = -p_1(0 - V_1)$ . The work done on the right side is:  $w_2 = -p_2(V_2 - 0)$ .

The total work done is then:

$$w = p_1V_1 - p_2V_2 \quad (1)$$

Since the process is adiabatic, the total change in  $U$  is just the work, or

$$\Delta U = U_2 - U_1 = p_1V_1 - p_2V_2 \quad (2)$$

$$U_2 + p_2V_2 = U_1 + p_1V_1 \quad (3)$$

so that:

$$H_2 = H_1 \quad (4)$$

and the process is **isoenthalpic**.

### 4. The Joule-Thomson Coefficient

What is measured experimentally is

$$\mu_{JT} = \lim_{\Delta p \rightarrow 0} \frac{T_2 - T_1}{p_2 - p_1} \quad (5)$$

which becomes, taking into account that the process is isoenthalpic:

$$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H \quad (6)$$

All that we've done so far is reduced the experiment to mathematics. The experimental result is that  $\mu_{JT}$  is sometimes positive and sometimes negative. In fact it is found that there is a certain temperature called the **inversion temperature** such that if the initial temperature  $T_1$  is *above* the inversion temperature, the final temperature is *higher* than the initial temperature. If the initial temperature is *below* the inversion temperature, the final temperature is *lower* than the initial temperature. The inversion temperature is found, experimentally, to depend on the pressure.

To understand this we need to relate  $\mu_{JT}$  to quantities that are experimentally measurable.<sup>4</sup>

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<sup>4</sup> The ability to do this is one of the main points of thermodynamics.

To do this we can start with the total differential of  $H$  assuming that  $T$  and  $p$  are the independent variables:

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad (7)$$

Now our process is isoenthalpic, so  $dH = 0$ . This gives:

$$0 = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad (8)$$

Now I divide through by  $dp$  at constant  $H$  to get:<sup>5</sup>

$$\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H + \left(\frac{\partial H}{\partial p}\right)_T \quad (9)$$

Note the subscript  $H$  at the appropriate point in eq. (9). Lastly, let us solve for  $(\partial T/\partial p)_H$  to get:

$$(\partial T/\partial p)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} \quad (10)$$

This result simplifies a bit right away. We know that  $(\partial H/\partial T)_p$  is the heat capacity  $C_p$ , so:

$$(\partial T/\partial p)_H = -\frac{(\partial H/\partial p)_T}{C_p} \quad (11)$$

but we can't make it any simpler. We need to express  $(\partial H/\partial p)_T$  in terms that can be measured. Indeed, this can be done, but it requires one slight bit of magic. A result that will be proven later<sup>6</sup>

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \quad (12)$$

which, when used in eq. (11) gives:

$$\Gamma = \frac{T(\partial V/\partial T)_p - V}{C_p} \quad (13)$$

a neat equation in which *all* of the quantities are measurable.

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<sup>5</sup> This is a touchy point. Pure mathematicians would perhaps object to treating an infinitesimal as if it were a finite quantity. But this procedure of dividing by  $dx$  (where here  $x = p$ ) in thermodynamic equations *can* be justified mathematically and we do it all the time. Perhaps the best way to think of it is to think of  $dp$  (or whatever) as actually representing a very small, but finite change in pressure. Then at the very end let all infinitesimal ratios go to their limits.

<sup>6</sup> They always say this, right?

So we come to the end of the theory with a formula but no explanation. It all seems to depend on how the volume of the gas changes with temperature and on the heat capacity. How can we learn anything more? Well, we can look at *model* gases, that is, gases for which we know the equation of state. Looking at some of these may tell us something.

## 5. The Joule-Thomson Coefficient for Model Gases

If we knew the equation of state for a gas, we could *calculate* the Joule-Thomson coefficient. For instance, for an ideal gas  $(\partial V/\partial T)_p = V/T$ , so

$$\mu_J = 0 \quad \text{ideal gas} \quad (14)$$

Ideal gases are boring.

But they have told us something. There is *no* Joule-Thomson effect for an ideal gas at all. And how do ideal gases differ from real gases? They have no interactions at all. No attractions and no repulsions. But that's the only way in which they differ. So we conclude that *the Joule-Thomson effect depends on the interactions between gas molecules.*

A gas obeying van der Waals equation will prove more interesting. Since we can't solve van der Waals equation for  $V$  explicitly<sup>7</sup> we have to use an approximation. A convenient one is eq 1.10a in Atkins. This can be written

$$Z = 1 + \frac{1}{RT} \left( b - \frac{a}{RT} \right) p + \dots \quad (15)$$

which is the first two terms of the *virial equation* approximation for a van der Waals gas.

We want to take this expression, solve it for  $\bar{V}$ , and then differentiate it to get  $(\partial V/\partial T)_p$ . With this available we can plug into eq. (13) and calculate  $\mu_J$ .

Now since  $Z = p\bar{V}/RT$ , we can solve eq. (15) for  $V$  to get:

$$\bar{V} = \frac{RT}{p} + \left( b - \frac{a}{RT} \right) + \dots \quad (16)$$

What we want is  $(\partial V/\partial T)_p$ . From eq. (16) we get:

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{p} + \frac{a}{RT^2} + \dots \quad (17)$$

Now this has to be multiplied by  $T$ . This gives:<sup>8</sup>

<sup>7</sup> It's a cubic in  $V$ , remember?

<sup>8</sup> I'm showing all the steps. Nobody expects you to memorize this stuff. Just read it and learn *where* the Joule-Thomson effect comes from.

$$T\left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{p} + \frac{a}{RT} + \dots \quad (18)$$

And now subtracting  $\bar{V}$  as given in eq. (16) we get (after some cancellations):

$$T\left(\frac{\partial V}{\partial T}\right)_p - \bar{V} = -\left(b - \frac{2a}{RT}\right) + \dots \quad (19)$$

and so, finally, the Joule-Thomson coefficient for a gas obeying van der Waals equation is:

$$\mu_{JT} = \frac{\frac{2a}{RT} - b}{C_p} + \dots \quad (20)$$

OK, you can't tell much from this equation all by itself except that it certainly looks messy. But there is a way theoreticians handle things like this: they look at the extremes. Let's see what happens to the Joule-Thomson coefficient when the temperature gets very low. That is, what is the limit when  $T$  goes to 0? Well, as  $T$  goes to 0, all terms with  $T$  in the denominator get very large. So the term involving  $2a/RT$  gets much larger than  $b$ . And the  $b$  term can be neglected at very low temperatures.

$$\mu_{JT} = \frac{2a}{RTC_p} + \dots \quad (\text{very low temperature}) \quad (21)$$

which is clearly *positive* since every term in it is positive. This agrees with experiment. A positive Joule-Thomson coefficient means *cooling*. But also note that the resulting expression only contains the van der Waals  $a$ . All of the terms involving  $b$  have gone away at low temperature.

We can also look at what happens when  $T$  gets very large. This result is quite simple since all terms containing a  $T$  in the denominator go to zero. The result is:

$$\mu_{JT} = -\frac{b}{C_p} \quad (\text{very high temperature}) \quad (22)$$

and that's very interesting. First, it agrees with experiment since it is *negative*, meaning *heating*. Second, notice that all of the terms involving van der Waals  $a$  have now vanished, leaving only  $b$ .

Lastly, it should be pointed out that there is one way in which eq. (20) *does not* agree with experiment. Eq. (20) predicts an *inversion temperature* of:

$$T_{\text{inversion}} = \frac{2a}{bR} \quad (\text{van der Waals gas}) \quad (23)$$

which is gotten by setting  $\mu_{JT}$  equal to zero in eq. (20). The problem is that this inversion temperature is not a function of the pressure. Experimentally the inversion temperature is a function of the pressure. If we'd carried one more term in eq. (15) we would have had a (much more messy) result that is a function of pressure.

## 6. Conclusions

So what can we conclude? Several things. First, since  $J_T$  is positive at low temperatures and negative at high temperatures, it must have an inversion temperature. Second, the effect seems to depend (as we expected) on the attractive and repulsive forces acting between molecules. At low temperatures the *attractive* forces predominate.<sup>9</sup> At high temperatures the *repulsive* forces predominate.<sup>10</sup> So the Joule-Thomson effect can be explained this way: At low temperatures the intermolecular attraction is the most important interaction. When the cold gas is expanded, the average distance between molecules is increased. This means that the molecules are pulled apart. Since they attract each other this *takes* energy. And since the process is adiabatic, the only source of energy is the internal energy of the gas itself. So, with the internal energy reduced, the gas *cools*.

On the other hand, at high enough temperatures the predominant interaction is *repulsion*. The gas wants to separate. It wants to expand. When it does expand energy is obtained as the molecules separate. This *increases* the internal energy of the gas. And the gas *heats*.

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<sup>9</sup> Remember,  $a$  accounts for the attractions between molecules in van der Waals equation.

<sup>10</sup> The ones associated with  $b$ .