CHAPTER 10
THE JOULE AND JOULE-THOMSON EXPERIMENTS

10.1 *Introduction*

Equation 8.4.3, $TV^{\gamma-1} = \text{constant}$, 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.

10.2 *The Joule Experiment*

In Joule's original experiment, there was a cylinder filled with gas at high pressure connected via a stopcock to a second cylinder with gas at a low pressure – sufficiently low that, for the purpose of understanding the experiment, we shall assume the second cylinder to be entirely empty. The two cylinders were immersed in a water bath, and the stopcock was opened so that gas from the high-pressure cylinder flowed into the evacuated cylinder. No heat was supplied to or lost from the system, nor did the gas do any work, so the *internal energy* was constant during the expansion. Joule found no temperature fall as a result of the expansion. This, as we have argued in Section 10.1, is exactly what we would expect for an ideal gas; that is, for an ideal gas, the temperature is independent of the volume if the internal energy is constant. That is, for an ideal gas,

$$\left(\frac{\partial T}{\partial V}\right)_U = 0. \qquad\qquad 10.2.1$$

For a real gas, however, we would expect a small drop in temperature, and $\left(\dfrac{\partial T}{\partial V}\right)_U$, which is called the *Joule coefficient*, is not zero. The heat capacity of the water bath and the cylinders in Joule's original experiment, however, was too large for him to detect any fall of temperature even with a real gas. More sensitive experiments since have indeed detected a small cooling of a real gas.

We should be able to derive an expression for the Joule coefficient, given the equation of state, and we should also be able to show that, if the equation of state is the equation of state for an ideal gas, the Joule coefficient is zero.

Internal energy and enthalpy are both functions of state; that is, they are functions of *P*, *V* and *T*. However, any particular substance cannot exist at any arbitrary point in *PVT*-space, but is constrained to be on the two-dimensional surface represented by its *equation of state*. Figures VI.7, 8 and 9 of Chapter 6 represent an example of such a surface. In other words, *P*, *V* and *T* cannot be varied independently; they are connected by an equation of the form *f*(*P*, *V*,*T*) = 0. Thus internal energy and enthalpy can be described by a function of just two of the state variables *P*, *V* and *T*.

In the experiment we are discussing, we are interested in how temperature varies with volume in an experiment in which the internal energy is constant. We shall therefore choose *U* as our state function and *V* and *T* as our independent state variables. That is, we shall write $U = U(V,T)$, so that

$$\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T = -1. \qquad 10.2.2$$

Our aim, of course, is to find an expression for the Joule coefficient $\left(\dfrac{\partial T}{\partial V}\right)_U$, for which I shall be using the symbol η.

The second of these partial derivatives is C_V, and therefore

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T. \qquad 10.2.3$$

Now $$dU = TdS - PdV. \qquad 10.2.4$$

That is, $$dS = \frac{1}{T}\left[dU + PdV\right] = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV\right]. \qquad 10.2.5$$

$$dS = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV + \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT. \qquad 10.2.6$$

But we also have

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT.$$ 10.2.7

Therefore

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$ 10.2.8

and

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V.$$ 10.2.9

The mixed second derivatives are

$$\frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \frac{1}{T}\left[\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial P}{\partial T}\right)_V\right]$$ 10.2.10

and

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}.$$ 10.2.11

But entropy is a function of state and dS is an exact differential, so the mixed second derivatives are equal. Whence, after simplification:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$ 10.2.12

Hence, returning to equation 10.2.3, we obtain, for the Joule coefficient,

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right].$$ 10.2.13

Trivial Exercise: Show that, for an ideal gas, the Joule coefficient is zero.

Exercise: Show that, for a van der Waals gas, the Joule coefficient is

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V V^2}.$$ 10.2.14

Hence, for a finite volume change,

$$T_2 = T_1 - \frac{a}{C_V}\left(\frac{1}{V_1} - \frac{1}{V_2}\right).$$ 10.2.15

For example, the volume of a kmole of CO_2 at a temperature of 20 °C (293.15 K) and a pressure of 1 atm (1.013×10^5 Pa) is $V_1 = RT/P = 24.06$ m^3. (That's a lot of cubic metres – but then 44 kg of CO_2 is a lot of carbon dioxide.). If its volume were doubled to 48.12 m^3 in an irreversible Joule-type expansion, what would be its new temperature? From Chapter 6, we find $a = 3.7 \times 10^5$ Pa m^6 kmole^{-1}, and from Chapter 8 we find that $C_P = 37100$ J kmole^{-1} K^{-1} and therefore let's take $C_V = 28786$ J kmole^{-1} K^{-1}, and so we obtain $T_2 = 292.88$ K $= 19.73$ °C. This cooling is a result not of the gas doing external work as in a reversible adiabatic expansion, but of doing work against the internal van der Waals forces between the molecules. What would be the temperature drop in a reversible adiabatic expansion? The new temperature would be given by $T_2 = \left(\dfrac{V_1}{V_2}\right)^{\gamma-1} T_1$. Let's take $\gamma = 37100 \div 28786 = 1.29$. Then $T_2 = (1/2)^{0.29} \times 293.15 = 239.77$ K $= -33.38$ °C at which temperature it would easily have sublimated into solid CO_2. In this calculation, I used $C_P - C_V = R$ and $TV^{\gamma-1} = $ constant, which are valid only for an ideal gas. We'll shortly derive a more general expression for $C_P - C_V$, but the correction for nonideality will obviously be quite small.

10.3 *The Joule-Thomson Experiment*

The experiment is also known as the Joule-Kelvin experiment. William Thomson was created Lord Kelvin. The experiment is also known as the porous plug experiment.

In the Joule-Thomson experiment a constant flow of gas was maintained along a tube which was divided into two compartments separated by a porous plug, such that the pressure and molar volume on the upstream side were P_1, V_1, and the pressure and molar volume on the downstream side were P_2, V_2. Under such circumstances the **net** work done **on** a mole of gas in passing from one compartment to the other is $P_1V_1 - P_2V_2$. (Imagine, for example, that a piston pushes a mole of gas towards the plug from the upstream side, through a distance x_1; if A is the cross-sectional area of the tube, the work done **on** the gas is $P_1Ax_1 = P_1V_1$. Imagine also that the gas on the downstream side pushes a piston away from the plug through a distance x_2. The work done **by** the gas is $P_2Ax_2 = P_2V_2$. Therefore the net external work done **on** the gas is $P_1V_1 - P_2V_2$.) If no heat is supplied to or lost from the system, the increase in internal energy of this gas is just equal to this work done on it:

$$U_2 - U_1 = P_1V_1 - P_2V_2 ,$$

or
$$U_1 + P_1V_1 = U_2 + P_2V_2 . \qquad\qquad 10.3.1$$

That is, there is no change in enthalpy. Therefore, we want to find $\left(\dfrac{\partial T}{\partial P}\right)_H$, which is the *Joule-Thomson coefficient,* for which I shall be using the symbol μ.

In the experiment we are discussing, we are interested in how temperature varies with pressure in an experiment in which the enthalpy is constant. We shall therefore choose H as our state function and P and T as our independent state variables. That is we shall write $H = H(P,T)$, so that

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial H}\right)_T = -1. \qquad 10.3.2$$

The second of these partial derivatives is C_P, and therefore

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T. \qquad 10.3.3$$

Now

$$dH = TdS + VdP. \qquad 10.3.4$$

That is,

$$dS = \frac{1}{T}[dH - VdP] = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT - VdP\right]. \qquad 10.3.5$$

$$dS = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT. \qquad 10.3.6$$

But we also have

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT. \qquad 10.3.7$$

Therefore

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \qquad 10.3.8$$

and

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P. \qquad 10.3.9$$

The mixed second derivatives are

$$\frac{\partial^2 S}{\partial T \partial P} = -\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - P\right] + \frac{1}{T}\left[\frac{\partial^2 H}{\partial T \partial P} - \left(\frac{\partial V}{\partial T}\right)_P\right] \qquad 10.3.10$$

and

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial P \partial T}. \qquad 10.3.11$$

But entropy is a function of state and dS is an exact differential, so the mixed second derivatives are equal. Whence, after simplification:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P. \qquad 10.3.12$$

Hence, returning to equation 10.3.3, we obtain, for the Joule-Thomson coefficient,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]. \qquad 10.3.13$$

Trivial Exercise: Show that, for an ideal gas, the Joule-Thomson coefficient is zero, and also that, for an ideal gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = 0. \qquad 10.3.14$$

This is analogous to equation 8.1.4 for an ideal gas, namely $\left(\dfrac{\partial U}{\partial V}\right)_T = 0.$

Exercise. Show that, for a van der Waals gas, the Joule-Thomson coefficient is

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{V}{C_P}\cdot\frac{\left(RTV^2b - 2a(V-b)^2\right)}{RTV^3 - 2a(V-b)^2}. \qquad 10.3.15$$

(Verify the dimensions of this expression.)

Hint: It is difficult to calculate $(\partial V / \partial T)_P$ directly, because it is difficult to express V explicitly as a function of P and T. It is not actually impossible to do it algebraically, because van der Waals' equation is a cubic equation in V, and a cubic equation does have an algebraic solution. It is easier, however, to calculate $(\partial V / \partial T)_P$ from $\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial P}{\partial T}\right)_V \Big/ \left(\dfrac{\partial P}{\partial V}\right)_T,$ or from $\left(\dfrac{\partial V}{\partial T}\right)_P = 1 \Big/ \left(\dfrac{\partial T}{\partial V}\right)_P.$

Note also that the Joule-Thomson coefficient may be negative or positive; i.e., it may result in cooling or heating. It will result in heating if you start above a certain temperature called the *inversion temperature*, and cooling if you start below the inversion temperature. The Joule-Thomson effect is used in the *Linde method* for cooling and ultimately liquefying gases. For most gases, the inversion temperature is higher than room temperature, so that cooling starts immediately. But for hydrogen, the inversion temperature is about $-80\ ^{\circ}$C, and hydrogen must be cooled below this temperature before the Joule-Thomson effect can be used to cool it further and to liquefy it. You can see from equation 10.3.14 that the inversion temperature for a van der Waals gas is equal to $\dfrac{2a(V - b)^2}{RV^2b} \approx \dfrac{2a}{Rb}.$ Here V is the molar volume.

Summary:

Joule coefficient $\qquad \eta = \left(\dfrac{\partial T}{\partial V}\right)_U = \dfrac{1}{C_V}\left[P - T\left(\dfrac{\partial P}{\partial T}\right)_V\right].$ $\qquad$ 10.2.13

Joule-Thomson coefficient $\quad \mu = \left(\dfrac{\partial T}{\partial P}\right)_H = \dfrac{1}{C_P}\left[T\left(\dfrac{\partial V}{\partial T}\right)_P - V\right].$ $\qquad$ 10.3.13

10.4 C_P *Minus* C_V

In Section 8.1 we pointed out that the heat capacity at constant pressure must be greater than the heat capacity at constant volume. We also showed that, for an ideal gas, $C_P = C_V + R$, where these refer to the molar heat capacities. We said that in Chapter 10 we would try and develop a more general expression for $C_P - C_V$, which was applicable in general and not only for an ideal gas. Some of the relations that we developed in Sections 10.2 and 10.3 give us the opportunity to try to do that now.

Let us consider an isobaric process and express the internal energy U as a function of V and T. (As we have pointed out, P, V and T are not independent variables because they are connected through the equation of state, so we may choose any two of them as independent variables.) Then, if the volume and temperature increase by infinitesimal amounts, the corresponding increase in the internal energy is given by

$$dU = \left(\dfrac{\partial U}{\partial V}\right)_T dV + \left(\dfrac{\partial U}{\partial T}\right)_V dT. \qquad 10.4.1$$

I.e., $\qquad\qquad\qquad\qquad dU = \left(\dfrac{\partial U}{\partial V}\right)_T dV + C_V dT. \qquad\qquad 10.4.2$

Consider now the first law:

$$dU = dQ + dW. \qquad 10.4.3$$

In an isobaric process, $dQ = C_P\, dT$, and in a reversible process, $dW = -P\, dV$.

Therefore $\qquad\qquad C_P dT - PdV = \left(\dfrac{\partial U}{\partial V}\right)_T dV + C_V dT. \qquad 10.4.4$

Divide by dT, recalling that we are considering an isobaric process:

$$C_P - P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + C_V.$$

10.4.5

Hence

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P.$$

10.4.6

This is a useful general expression, as long as we know or can determine $(\partial U / \partial V)_T$.

(Note that the extensive quantities can be total, specific or molar.)

Let us just test this by applying it to an ideal gas to see if it produces the result that it ought to produce. For an ideal gas, the internal energy at a given temperature is independent of the volume. This is because in an ideal gas there are no intermolecular forces, so that, as the volume increases and the intermolecular distances increase, there is no change in potential energy; and, if the temperature is constant, so is the kinetic energy. Thus, for an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$. The volume of a mole of ideal gas is $V = RT/P$, so that $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$.

Therefore

$$C_P - C_V = P \times \frac{R}{P} = R,$$

10.4.7

and all is well.

For any substance other than an ideal gas, we shall need to know $\left(\frac{\partial U}{\partial V}\right)_T$ before we can make use of equation 10.4.6. But equation 10.2.12, which we developed in Section 10.2 while analysing the Joule effect, enables us to do just this:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

10.2.12

On combining this with equation 10.4.6, we obtain

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

10.4.8

Depending on the equation of state, it may or may not be easy to evaluate these partial derivatives. For example, for the van der Waals equation of state (which is a cubic equation in V), it is not easy to evaluate $(\partial V / \partial T)_P$ directly, but one can then make use of $(\partial V / \partial T)_P = -(\partial T / \partial V)_P$ or of

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \quad \text{in order to get} \quad C_P - C_V \text{ in terms of easily evaluable partial}$$

derivatives. For example

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \bigg/ \left(\frac{\partial T}{\partial V}\right)_P \quad \text{or} \quad -T\left(\frac{\partial P}{\partial T}\right)_V^2 \bigg/ \left(\frac{\partial P}{\partial V}\right)_T \qquad 10.4.9$$

or several other variants.

Any of equations 10.4.8 or 10.4.9 can be used to calculate $C_P - C_V$; it just depends on which of the derivatives, for a particular equation of state, are easiest to calculate.

The reader will easily be able to show that, for a mole of an ideal gas, this becomes just $C_P - C_V = R$. A little more algebra will be needed to show that, for a mole of a van der Waals gas,

$$C_P - C_V = \frac{R}{1 - 2a(V-b)^2/(RTV^3)} = R \cdot \frac{P + a/V^2}{P - a/V^2 + 2ab/V^3} \approx R \cdot \frac{(RT)^2 + aP}{(RT)^2 - aP}. \qquad 10.4.10$$

In the above analysis, we considered an isobaric process and we chose the internal energy as our function of state and we started by calculating the increment in U corresponding to increments dV and dT in the volume and temperature. It is tempting now to go through the same analysis, but this time to consider an isochoric process and to choose the enthalpy as our function of state. We start by calculating the increment in H corresponding to increments dP and dT in the pressure and temperature:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT. \qquad 10.4.11$$

I.e.,
$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT. \qquad 10.4.12$$

Now $H = U + PV$, $\therefore dH = dU + PdV + VdP = dQ + dW + PdV + VdP$.

Provided that we include in dQ any irreversible work that is being done on the system (irreversible work has the same effect, as we have seen, as adding heat), so that $dW = -PdV$, then

$$dH = VdP + dQ = VdP + C_V dT. \qquad 10.4.13$$

On comparison of equations 10.4.11 and 10.4.12 we obtain

$$VdP + C_V dT = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT. \qquad 10.4.14$$

Divide by dT, recalling that we are considering an isochoric process. From this, we obtain an alternative expression for the difference between the heat capacities:

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P} \right)_T \right]\left(\frac{\partial P}{\partial T} \right)_V.$$
                                                                    10.4.15

This is quite analogous to equation 10.4.6. It is left to the reader to show that, for an ideal gas, this reduces to $C_P - C_V = R$. This will be easy if you recall equation 10.3.14, for an ideal gas:

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

For any substance other than an ideal gas, we shall need to know $\left(\frac{\partial H}{\partial P} \right)_T$ before we can make use of equation 10.4.15. But equation 10.3.12, which we developed in Section 10.3 while analysing the Joule-Thomson effect, enables us to do just this:

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T\left(\frac{\partial V}{\partial T} \right)_P.$$
                                                                    10.3.12

On combining this with equation 10.4.15, we obtain again equation 10.4.8. We obtained no new result for $C_P - C_V$ (although we did obtain the important result 10.4.16 for an ideal gas), but it is satisfying and instructive to have obtained the same result via internal energy and via enthalpy.

After this, we can hardly resist the temptation to see what happens if we treat P and V as independent variables. Thus, if $U = U(P,V)$, then increases of dP and dV in the pressure and volume result in an increase dU of the internal energy given by

$$dU = \left(\frac{\partial U}{\partial P} \right)_V dP + \left(\frac{\partial U}{\partial V} \right)_P dV.$$
                                                                    10.4.17

But we already know (equation 10.4.1), by choosing the independent variables to be T and V, that

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT.$$
                                                                    10.4.1

And from the equation of state $T = T(P,V)$, we derive that

$$dT = \left(\frac{\partial T}{\partial P} \right)_V dP + \left(\frac{\partial T}{\partial V} \right)_P dV.$$
                                                                    10.4.18

By elimination of dT from equations 10.4.1 and 10.4.18 we obtain

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial V}\right)_T dV. \qquad 10.4.19$$

On comparison of equations 10.4.17 and 10.4.19 we deduce the following relations, which are occasionally useful:

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V, \qquad 10.4.20$$

(which I hope we already knew!)

and
$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T. \qquad 10.4.21$$

The first of these is, of course, trivial, and does not require this lengthy derivation. The second is a worthwhile relation, which we may occasionally find useful.

Summary:

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad 10.4.6, \ 10.4.15$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and variants.} \qquad 10.4.8$$

10.5 *Blackbody Radiation*

Before we forget all the equations in this chapter, let's use equation 10.2.12 (which we have already used twice – once in the derivation of the Joule-Thomson coefficient and once in the derivation of $C_P - C_V$) in a totally different application:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \qquad 10.2.12$$

This is a very general thermodynamical relation, and is by no means restricted to Joule's experiment. Let us apply it to electromagnetic radiation (rather than molecules) in an enclosure.

You may already have studied the theory of radiation in a cavity and the closely-related theory of blackbody radiation. You will know that classical electromagnetic theory failed to explain the observed characteristics of blackbody radiation, and that it was not explained fully until the advent of quantum theory. In the middle of the nineteenth century Kirchhoff argued theoretically that the

energy density inside a cavity was independent of the nature of the walls of the cavity and depended only on the temperature and the wavelength. Stefan had shown experimentally that the radiation density inside a cavity integrated over all wavelengths was proportional to the fourth power of the temperature. Later on, Lummer and Pringsheim did some detailed measurements which showed how the radiation density per until wavelength varied with wavelength and temperature. It was shown by Rayleigh and Jeans that classical electromagnetic theory failed badly at short wavelengths to explain the observed distribution of the cavity radiation with wavelength. In 1900 Planck, without quite knowing why, showed that, if he regarded radiation as being made up of quanta of energy $h\nu$, the energy density per unit volume per unit wavelength interval would be expected to vary as $u_\lambda = \dfrac{C_1}{\lambda^5 (e^{C_2/(\lambda T)} - 1)}$, which agreed very well with the experimental data of Lummer and Pringsheim. You also may know that if you integrate this expression over all wavelengths (not particularly easy), you find that $\int u_\lambda d\lambda$ is proportional to T^4, thus also agreeing with the observations of Stefan.

However, although quantum theory was necessary to explain the Lummer-Pringsheim measurements of how u_λ varies with temperature, Boltzmann used classical thermodynamical theory to explain Stefan's T^4 law almost immediately after Stefan had announced his results, and long before the advent of quantum theory.

The theory of radiation tells us that the radiation energy per unit volume u depends only on the temperature (this is Kirchhoff's radiation law) and that the radiation pressure P is related to the energy per unit volume by $P = \frac{1}{3}u$. The derivation of this is very similar to the expression that we derived for the pressure of molecules in a gas. For this situation, equation 10.2.12 becomes

$$u = \tfrac{1}{3}T\frac{du}{dT} - \frac{u}{3}, \qquad\qquad 10.5.1$$

or
$$4u = T\frac{du}{dT}. \qquad\qquad 10.5.2$$

Integration of this (do it!) shows that $u \propto T^4$, without any need for quantum theory.

This is often written as $u = aT^4$, but beware, here a is not what it generally known as "Stefan's constant". See Chapters 1 and 2 (especially Section 1.17) of my Stellar Atmospheres notes for more on this. Stefan's Law generally refers to the *exitance* of a black body surface, $M = \sigma T^4$, whereas here we are referring to the energy density of radiation in a cavity. The relation between a and Stefan's constant σ is $a = 4\sigma/c$.

Now suppose that you had some radiation at temperature T in an enclosure (such as The Universe) of volume V. And suppose that volume were to expand adiabatically, thus diluting the energy density. What would be the new temperature? In what follows, V means the volume (not the "specific" or "molar" volume) of the enclosure. U is the internal energy of the radiation inside it,

and u is the radiation energy density, such that $U = uV$, and we shall be making use of $P = \frac{1}{3}u$ and of $u = aT^4$.

If the volume were to increase by dV at pressure P, the work done by the radiation would be $PdV = \frac{1}{3}udV$, and, if we assume that the expansion is adiabatic, this results (by the first law of thermodynamics) in a decrease of the internal energy. We apply the first law: $dU = -PdV$. That is

$$d(uV) = udV + Vdu = -\tfrac{1}{3}udV. \qquad\qquad 10.5.3$$

$$\frac{dV}{V} = -\frac{3}{4}\frac{du}{u}. \qquad\qquad 10.5.4$$

Therefore $\qquad\qquad V \propto u^{-3/4} \quad\text{or}\quad u \propto V^{-4/3}. \qquad\qquad 10.5.5$

But $u \propto T^4$, and hence $\qquad\qquad VT^3 \text{ is constant,} \qquad\qquad 10.5.6$

or the temperature is inversely proportional to the linear dimensions of the enclosure.