EXPANSIONS AND COMPRESSIONS OF AN IDEAL GAS

Since you have already *read* about the heat capacity of a gas, which characterizes how its temperature changes when heat is added, we can more easily consider how to characterize the way gases can expand or contract. We will make calculations for an ideal gas that will typically be accurate at the level of about 1% for most real gases.

Recall that heat input to a gas may take place under a variety of conditions, but the text only considered two *special cases*: heat input at constant volume and heat input at constant pressure. Similarly, expansions come in many flavors, but we will discuss just two types …

- *Isothermal* expansions… in which the temperature doesn't change.
- *Adiabatic* expansions… in which no heat flows into or out of the gas.

We will look at each of these, in turn, in some detail. Before we do that let's look at what we expect to happen.

Q 1. A fixed amount of gas expands from volume V_i to V_f, starting at an initial pressure P_f. Let's consider doing two experiments, in one the gas expands isothermally, in the other it expands adiabatically.

- In which case is the final pressure higher?
- In which case does the gas do more work?

Pressure, P

V_i V_f
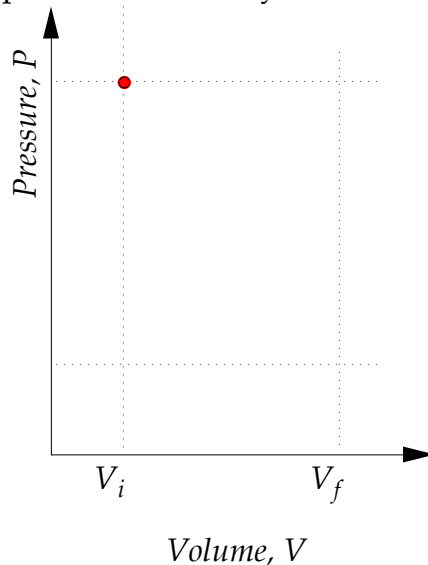
Volume, V

Isothermal Expansion

In both expansions we assume that at all times the gas is in *equilibrium*. Assuming this allows us to know that whatever the gas is doing, its pressure, volume and temperature are related by...

$$................................$$ (1)

In an isothermal expansion, the temperature is by definition constant, and so the pressure and volume are related by...

$$PV = constant \quad i.e. \, P \propto \frac{1}{V}$$ (2)

So we can easily evaluate the work done in expanding from V_i to V_f by remembering that the work done in a process <u>is the *area* under the *PV* curve</u>, or more technically is given by...

$$................................$$ (3)

All we need to do then is to substitute for P in the above equation and integrate. Easy! You will need to remember the perfect gas equation...

$$............................$$ (4)

and that...

$$\int_a^b \frac{1}{x} dx = \ln(x)\Big|_b - \ln(x)\Big|_a$$ (5)

So, it is now easy to evaluate the work done by z moles of gas during the expansion from V_i to V_f. Please take 6.38 minutes to show that...

$$\boxed{W = zRT\ln\left[\frac{V_f}{V_i}\right]}$$ (6)

and to solve the example problem below:

Q2. Two moles of air expands at constant temperature (300K) from an initial volume of 0.01 m³ (10 liters) to a final volume of 0.02 m³ (20 liters). Assuming air to behave like an ideal gas at this temperature and pressure, evaluate...

- the initial pressure,
- the final pressure,
- the work done during the expansion.

Data R=8.31 JK⁻¹mol⁻¹ $W = zRT\ln\left[\dfrac{V_f}{V_i}\right]$

Adiabatic Expansions

Adiabatic expansions are slightly more complicated, because the temperature does not stay constant during the expansion. However the principle is still the same. We want to find an expression that will relate P and V during an adiabatic expansion. Once we find this we will be able to use it to evaluate the integral...

$$W = \int_{V_i}^{V_f} P \mathrm{d}V . \qquad (7)$$

The reason for this worksheet is that I want you to have good notes on this argument. We combine the three expressions that we know about ideal gases...

- $PV = zRT$ (obviously)
- $\Delta U = \Delta Q - \Delta W$ (First Law of thermodynamics)
- $C_P - C_V = R$ (This comes from Eq. 5.40 of your text) where C_P and C_V are the _molar_ heat capacities of the ideal gas.

Consider what the First Law has to say about z moles of ideal gas that expands adiabatically by a small amount ΔV

- $\Delta Q = $ .... (I know it seems lame to have you fill in these blanks, but it will help you to _retain_ the formula in its proper form).

- $\Delta U = zC_v \Delta T$ by the definition of C_V.

- $\Delta W = P \Delta V$

Substituting these into the first law yields...

$$zC_v \Delta T = 0 - P \Delta V \qquad (8)$$

or

$$-\frac{zC_v}{P} = \frac{\Delta V}{\Delta T} \qquad (9)$$

Taking the limit as ΔV tends to $\mathrm{d}V$

$$\boxed{\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{-zC_V}{P}} \qquad (10)$$

Now consider the ideal gas law, and differentiate it with respect to T

$$\frac{d}{dT}(PV) = \frac{d}{dT}(zRT) \tag{11}$$

Both P and V change with T and so we use the product rule to write...

$$P\frac{dV}{dT} + V\frac{dP}{dT} = zR \tag{11}$$

We use the chain-rule of differentiation to rewrite the second term...

$$P\frac{dV}{dT} + V\frac{dP}{dV}\frac{dV}{dT} = zR \tag{11}$$

Rearranging this and substituting for dV/dT from the first part of the argument...

$$\frac{dV}{dT}\left[P + V\frac{dP}{dV}\right] = zR \tag{11}$$

$$\frac{-zC_V}{P}\left[P + V\frac{dP}{dV}\right] = zR \tag{12}$$

If we now simplify and collect terms...

$$-zC_V - zC_V\frac{V}{P}\frac{dP}{dV} = zR \tag{13}$$

$$-zC_V\frac{V}{P}\frac{dP}{dV} = zR + zC_V \tag{14}$$

$$-zC_V\frac{V}{P}\frac{dP}{dV} = z(R + C_V) = zC_P \tag{15}$$

$$\frac{V}{P}\frac{dP}{dV} = -\frac{C_P}{C_V} \tag{16}$$

$$\boxed{\frac{V}{P}\frac{dP}{dV} = -\gamma} \tag{17}$$

We are now nearly there. We can see that this is what we were looking for... a relationship between P and V only. Unfortunately it is a differential equation and not the simple algebraic one we were able to use in the case of an isothermal expansion.

We will look briefly at the solution. First, we rewrite this equation...

$$\frac{V}{P}\frac{dP}{dV} = -\gamma \qquad (18)$$

$$\frac{dP}{P} = -\gamma\frac{dV}{V} \qquad (19)$$

If this equation is true then integrating both sides will also yield a true relationship.

$$\int_{P_i}^{P_f}\frac{dP}{P} = -\gamma \int_{V_i}^{V_f}\frac{dV}{V} \qquad (20)$$

Here we have assumed γ to be constant, which is true for an ideal gas, and approximately true for real gases. If we use the indefinite form of the integrals we find...

$$\ln(P) = -\gamma\ln(V) + constant \qquad (21)$$

$$\ln(P) + \gamma\ln(V) = constant \qquad (22)$$

$$\ln(P) + \ln(V^\gamma) = \ln(PV^\gamma) = constant \qquad (23)$$

$$\boxed{PV^\gamma = constant}...\text{for an adiabatic expansion} \qquad (24)$$

which may be compared with

$$\boxed{PV = constant}...\text{for an isothermal expansion} \qquad (25)$$

OK. So let's try considering the same sample of gas that we used in the isothermal example Q 2, starting it out at the same temperature and pressure, and seeing where it gets to if it expands adiabatically...

Q 3. Suppose 2 moles of air initially at 300K, expands adiabatically from an initial volume of 0.01 m³ to a final volume of 0.02 m³. Assuming air to behave like an ideal gas at these temperature and pressure, evaluate...
- the initial pressure,
- the final pressure,   **Data** R = 8.31 JK⁻¹mol⁻¹
- the final temperature,
- the work done during the expansion.

$PV^\gamma = constant$ $\gamma = 1.67$ (ideal gas)

$$\int_{P_i}^{P_f} \frac{dP}{P} = -\gamma \int_{V_i}^{V_f} \frac{dV}{V}$$

- Initial pressure

$$P = \frac{zRT}{V}$$

- Final pressure

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_f = P_i \left(\frac{V_i}{V_f} \right)^\gamma$$

- Final temperature

$$T_f = \frac{P_f V_f}{zR}$$

- Work done.

Clever students may evaluate the constant of integration to find the constant in $PV^\gamma = constant$ and can then substitute for P into $W = \int PdV$.
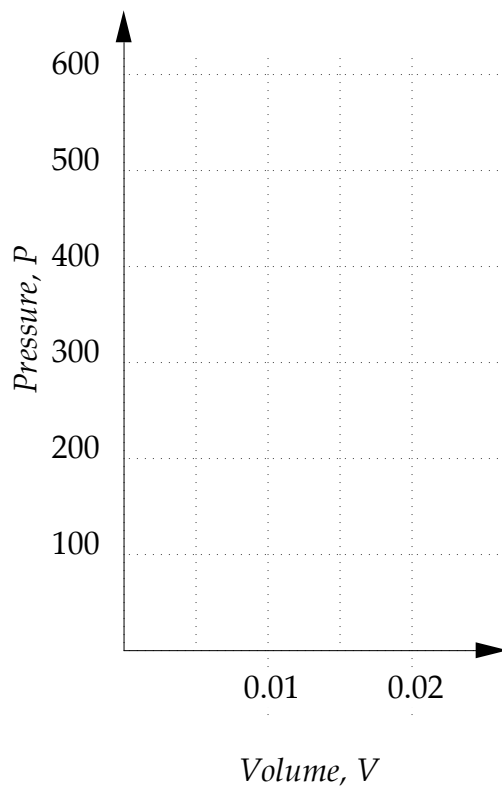
Laggardly students may simply recall that since the expansion is adiabatic, $\Delta Q = 0$, and hence by the First Law,

$$\Delta W = -\Delta U$$

$$\Delta W = -zC_V \Delta T$$

$$\Delta W = -z\frac{3}{2}R\Delta T \ \ (if \ p = 3)$$

Q 4. Plot the two expansions discussed this evening on the PV diagram below.

Q 5. If $PV^\gamma = constant$ during an adiabatic expansion, show that for an ideal gas, $TV^{\gamma-1}$ is also constant during an adiabatic expansion.