

TOPIC 2E Adiabatic changes

► Why do you need to know this material?

Adiabatic processes complement isothermal processes, and are used in the discussion of the Second Law of thermodynamics.

► What is the key idea?

The temperature of a perfect gas falls when it does work in an adiabatic expansion.

► What do you need to know already?

This Topic makes use of the discussion of the properties of gases (Topic 1A), particularly the perfect gas law. It also uses the definition of heat capacity at constant volume (Topic 2A) and constant pressure (Topic 2B) and the relation between them (Topic 2D).

The temperature falls when a gas expands adiabatically (in a thermally insulated container). Work is done, but as no heat enters the system, the internal energy falls, and therefore the temperature of the working gas also falls. In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls too.

2E.1 The change in temperature

The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as the sum of two steps (Fig. 2E.1). In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume it occupies (Topic 2A), the overall change in internal energy arises solely from the second step, the change in temperature at constant volume. Provided the heat capacity is independent of temperature, the change in the internal energy is

$$\Delta U = (T_f - T_i)C_V = C_V\Delta T$$

Because the expansion is adiabatic, $q = 0$; then because $\Delta U = q + w$, it follows that $\Delta U = w_{\text{ad}}$. The subscript 'ad' denotes an

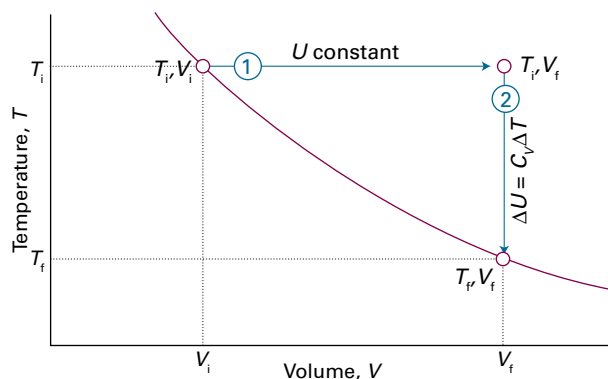


Figure 2E.1 To achieve a change of state from one temperature and volume to another temperature and volume, treat the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

adiabatic process. Therefore, by equating the two expressions for ΔU ,

$$w_{\text{ad}} = C_V\Delta T \quad \text{Work of adiabatic change [perfect gas]} \quad (2E.1)$$

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what is expected on molecular grounds, because the mean kinetic energy is proportional to T , so a change in internal energy arising from temperature alone is also expected to be proportional to ΔT . From these considerations it is possible to calculate the temperature change of a perfect gas that undergoes reversible adiabatic expansion (reversible expansion in a thermally insulated container).

How is that done? 2E.1 Deriving an expression for the temperature change in a reversible adiabatic expansion

Consider a stage in a reversible adiabatic expansion of a perfect gas when the pressure inside and out is p . When considering reversible processes, it is usually appropriate to consider infinitesimal changes in the conditions, because pressures and temperatures typically change during the process. Then follow these steps.

Step 1 Write an expression relating temperature and volume changes

The work done when the gas expands reversibly by dV is $dw = -pdV$. This expression applies to any reversible change, including an adiabatic change, so specifically $dw_{\text{ad}} = -pdV$. Therefore, because $dq = 0$ for an adiabatic change, $dU = dw_{\text{ad}}$ (the infinitesimal version of $\Delta U = w_{\text{ad}}$).

For a perfect gas, $dU = C_v dT$ (the infinitesimal version of $\Delta U = C_v \Delta T$). Equating these expressions for dU gives

$$C_v dT = -pdV$$

Because the gas is perfect, p can be replaced by nRT/V to give $C_v dT = -(nRT/V)dV$ and therefore

$$\frac{C_v dT}{T} = -\frac{nR dV}{V}$$

Step 2 Integrate the expression to find the overall change

To integrate this expression, ensure that the limits of integration match on each side of the equation. Note that T is equal to T_i when V is equal to V_i , and is equal to T_f when V is equal to V_f at the end of the expansion. Therefore,

$$C_v \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

where C_v is taken to be independent of temperature. Use Integral A.2 in each case, and obtain

$$C_v \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

Step 3 Simplify the expression

Because $\ln(x/y) = -\ln(y/x)$, the preceding expression rearranges to

$$\frac{C_v}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

Next, note that $C_v/nR = C_{v,m}/R = c$ and use $\ln x^a = a \ln x$ to obtain

$$\ln \left(\frac{T_f}{T_i} \right)^c = \ln \frac{V_i}{V_f}$$

This relation implies that $(T_f/T_i)^c = (V_i/V_f)$ and, upon rearrangement,

$$\left| T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \quad c = C_{v,m}/R \right| \quad (2E.2a)$$

Temperature change
[reversible adiabatic
expansion, perfect gas]

By raising each side of this expression to the power c and reorganizing it slightly, an equivalent expression is

$$V_i T_i^c = V_f T_f^c \quad c = C_{v,m}/R \quad (2E.2b)$$

Temperature change
[reversible adiabatic
expansion, perfect gas]

This result is often summarized in the form $VT^c = \text{constant}$.

Brief illustration 2E.1

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm³ to 1.00 dm³. The molar heat capacity of argon at constant volume is 12.47 J K⁻¹ mol⁻¹, so $c = 1.501$. Therefore, from eqn 2E.2a,

$$T_f = (298 \text{ K}) \times \left(\frac{0.50 \text{ dm}^3}{1.00 \text{ dm}^3} \right)^{1/1.501} = 188 \text{ K}$$

It follows that $\Delta T = -110 \text{ K}$, and therefore, from eqn 2E.1, that

$$w_{\text{ad}} = \{(0.020 \text{ mol}) \times (12.47 \text{ J K}^{-1} \text{ mol}^{-1})\} \times (-110 \text{ K}) = -27 \text{ J}$$

Note that temperature change is independent of the amount of gas but the work is not.

2E.2 The change in pressure

Equation 2E.2a may be used to calculate the pressure of a perfect gas that undergoes reversible adiabatic expansion.

How is that done? 2E.2 Deriving the relation between pressure and volume for a reversible adiabatic expansion

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so $pV = nRT$ can be used to write

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f}$$

However, $T_i/T_f = (V_f/V_i)^{1/c}$ (eqn 2E.2a). Therefore,

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i} \right)^{1/c}, \quad \text{so} \quad \frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}+1} = 1$$

For a perfect gas $C_{p,m} - C_{v,m} = R$ (Topic 2B). It follows that

$$\frac{1}{c} + 1 = \frac{1+c}{c} = \frac{R + C_{v,m}}{C_{v,m}} = \frac{C_{p,m}}{C_{v,m}} = \gamma$$

and therefore that

$$\frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\gamma} = 1$$

which rearranges to

$$\left| p_f V_f^{\gamma} = p_i V_i^{\gamma} \right| \quad (2E.3)$$

Pressure change
[reversible adiabatic
expansion, perfect gas]

This result is commonly summarized in the form $pV^{\gamma} = \text{constant}$.

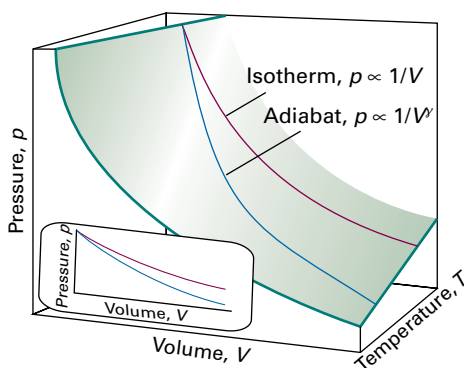


Figure 2E.2 An adiabat depicts the variation of pressure with volume when a gas expands adiabatically and, in this case, reversibly. Note that the pressure declines more steeply for an adiabat than it does for an isotherm because in an adiabatic change the temperature falls.

For a monatomic perfect gas, $C_{V,m} = \frac{3}{2}R$ (Topic 2A), and $C_{p,m} = \frac{5}{2}R$ (from $C_{p,m} - C_{V,m} = R$), so $\gamma = \frac{5}{3}$. For a gas of nonlinear polyatomic molecules (which can rotate as well as translate;

vibrations make little contribution at normal temperatures), $C_{V,m} = 3R$ and $C_{p,m} = 4R$, so $\gamma = \frac{4}{3}$. The curves of pressure versus volume for adiabatic change are known as **adiabats**, and one for a reversible path is illustrated in Fig. 2E.2. Because $\gamma > 1$, an adiabat falls more steeply ($p \propto 1/V^\gamma$) than the corresponding isotherm ($p \propto 1/V$). The physical reason for the difference is that, in an isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, the pressure does not fall as much as in an adiabatic expansion.

Brief illustration 2E.2

When a sample of argon (for which $\gamma = \frac{5}{3}$) at 100 kPa expands reversibly and adiabatically to twice its initial volume the final pressure will be

$$p_f = \left(\frac{V_i}{V_f}\right)^\gamma p_i = \left(\frac{1}{2}\right)^{5/3} \times (100 \text{ kPa}) = 31 \text{ kPa}$$

For an isothermal expansion in which the volume doubles the final pressure would be 50 kPa.

Checklist of concepts

- 1. The temperature of a gas falls when it undergoes an adiabatic expansion in which work is done.
- 2. An **adiabat** is a curve showing how pressure varies with volume in an adiabatic process.

Checklist of equations

Property	Equation	Comment	Equation number
Work of adiabatic expansion	$w_{\text{ad}} = C_v \Delta T$	Perfect gas	2E.1
Final temperature	$T_f = T_i (V_i / V_f)^{1/c}$	Perfect gas, reversible adiabatic expansion	2E.2a
	$c = C_{V,m} / R$		
	$V_i T_i^c = V_f T_f^c$		
Adiabats	$p_i V_i^\gamma = p_f V_f^\gamma$		2E.3
	$\gamma = C_{p,m} / C_{V,m}$		