

19-7 Internal Energy, $E_{int} = \frac{3}{2}nRT$: monatomic ideal gas

Assume that ideal gas is a monatomic gas (He, Ne, Ar - individual atoms) [not a molecule - H_2 , O_2 etc]

Assume that the internal energy E_{int} is the sum of the translational kinetic energies of the atoms.

(Quantum theory disallows rotational kinetic energy for individual atoms.)

For one mole of an ideal monatomic gas:

Internal energy, E_{int}
= kinetic energy, K + potential energy, U
E_{int} = K + U

 $E_{int} = K + 0$ U = 0 for free particles

 $E_{int} = K$

The average translational kinetic energy of a single atom depends only on the gas temperature and is given by, $K_{avq} = \frac{3}{2}kT$

For n moles of an ideal monatomic gas: Total number of atoms (in n moles), $N = n N_A$ and Boltzmann constant, $k = \frac{R}{N}$.

$$\mathsf{E}_{\mathsf{int}} = \mathsf{N} \; \mathsf{K}_{\mathsf{avg}} = (\mathsf{n} \; \mathsf{N}_{\mathsf{A}})(\frac{3}{2}k\mathsf{T}) = (\mathsf{n} \; \mathsf{N}_{\mathsf{A}})\{\frac{3}{2} \; (\frac{R}{N_A})\mathsf{T}\} = \frac{3}{2}\mathsf{n}\mathsf{R}\mathsf{T}$$

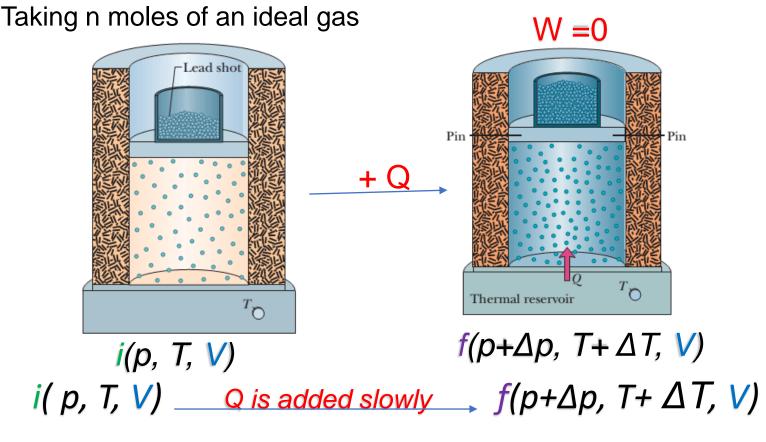
$$\Delta \mathsf{E}_{\mathsf{int}} = \frac{3}{2}\mathsf{n}\mathsf{R}\Delta\mathsf{T}$$

$$\Delta \mathsf{E}_{\mathsf{int}} = \frac{3}{2}\mathsf{n}\mathsf{R}\Delta\mathsf{T}$$

The internal energy E_{int} of an ideal gas is a function of the gas temperature *only*; it does not depend on any other variable.

19-7 Molar specific heat of a monatomic ideal gas at constant volume: $C_V = \frac{3}{2}R$

Molar Specific Heat at Constant Volume, C_V:



The heat Q is related to the temperature change ΔT by

$$Q = nC_V \Delta T$$
 [V = constant] [Q = mc ΔT]

1st law of thermodynamics:

$$\Delta E_{int} = Q - W = nC_V \Delta T - p\Delta V = nC_V \Delta T - p(V - V) = nC_V \Delta T - p(0) = nC_V \Delta T$$

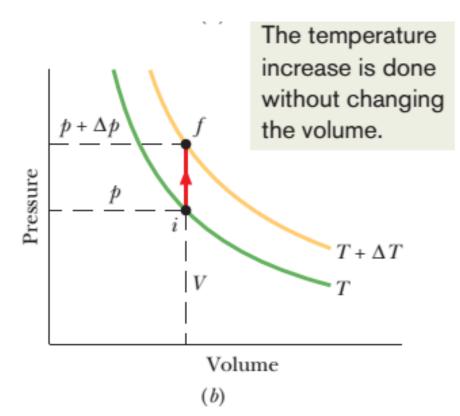


Figure 19-9 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-volume process. Heat is added, but no work is done. (b) The process on a p-V diagram.

$$\Delta E_{int} = nC_V \Delta T$$
 [but $\Delta E_{int} = \frac{3}{2}nR\Delta T$]

$$\frac{3}{2}$$
nR Δ T = nC_V Δ T

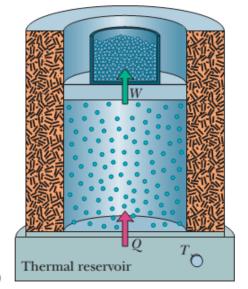
$$C_V = \frac{3}{2}R$$
 [monatomic gas]

$$C_V = \frac{3}{2}R = \frac{3}{2}(8.31) = 12.5 \text{ J/mol} - \text{K}$$
 [monatomic gas]

The C_V values for diatomic polyatomic gases are greater than for monatomic gases because the more complex molecules can rotate and thus have rotational kinetic energy.

Table 19-2 Molar Specific Heats at Constant Volume

Molecule	Examp	ole	C_V (J/mol·K)	
Monatomic	Ideal	$\frac{3}{2}R = 12.5$		
Wionatoline	Real	Не	12.5	
		Ar	12.6	
Diatomic	Ideal	$\frac{5}{2}R = 20.8$		
	Real	N_2	20.7	
		N_2 O_2	20.8	
Polyatomic	Ideal	3R = 24.9		
	Real	NH ₄	29.0	
		CO_2	29.7	



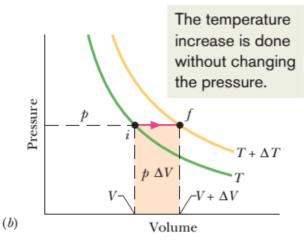


Figure 19-11 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constantpressure process. Heat is added and work is done in lifting the loaded piston. (b) The process on a p-V diagram. The work p ΔV is given by the shaded area.

19-7 Generalize $E_{int} = \frac{3}{2}nRT$ for monoatomic gas: $E_{int} = nCvT$ for any gas

We can now generalize $E_{int} = \frac{3}{2}nRT$ for the internal energy of any ideal gas by substituting $C_V = \frac{3}{2}R$.

$$E_{int} = \frac{3}{2}nRT$$

$$\mathsf{E}_{\mathsf{int}} = \mathsf{n}(\frac{3}{2}\mathsf{R})\mathsf{T} \qquad \left[\mathsf{C}_{\mathsf{V}} = \frac{3}{2}\mathsf{R}\right]$$

$$E_{int} = nC_VT$$
 [any ideal gas]

This equation applies not only to an ideal monatomic gas but also to diatomic and polyatomic ideal gases, provided the appropriate value of C_V is used.

When a confined ideal gas undergoes temperature change ΔT , then the resulting change in its internal energy is

$$\Delta E_{int} = nC_{V} \Delta T$$
 [ideal gas for any process]

"A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, not on what type of process produces the change".

No matter what path is actually taken between T and T+ Δ T, we can always use path 1 and Δ E_{int} = nC_V Δ T to compute Δ E_{int} easily.

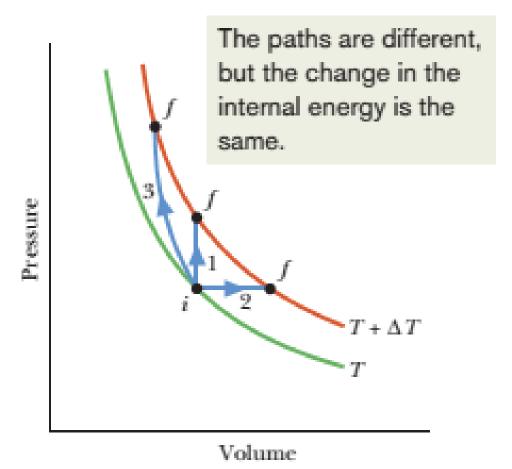


Figure 19-10 Three paths representing three different processes that take an ideal gas from an initial state i at temperature T to some final state f at temperature $T + \Delta T$.

19-7 Molar Specific Heat at Constant Pressure, C_D:

The temperature of our ideal gas is increased by the same small amount ΔT as previously but now the necessary energy (heat Q) is added with the gas under constant pressure.

$$i(p, T, V)$$
 Q is added slowly $f(p, T + \Delta T, V + \Delta V)$

The heat Q is related to the temperature change ΔT by

$$Q = nC_p \Delta T$$
 [p = constant]

Relation between molar specific heats C_D and C_V :

1st law of thermodynamics: $\Delta E_{int} = Q - W$ Ideal gas law: pV = nRT

$$\frac{\Delta}{\Delta T}(pV) = \frac{\Delta}{\Delta T}(nRT)$$

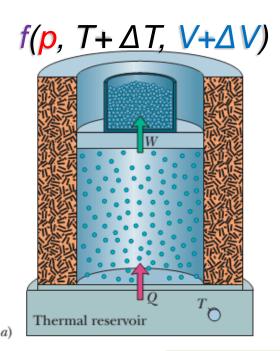
$$p\frac{\Delta V}{\Delta T} = nR\frac{\Delta T}{\Delta T}$$

$$p\frac{\Delta V}{\Delta T} = nR$$

$$p\frac{\Delta V}{\Delta T} = nR$$

$$p\Delta V = nR \Delta T$$

$$W = nR \Delta T$$



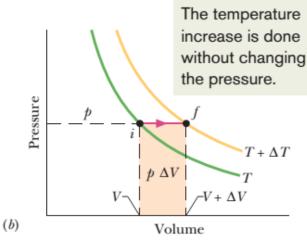


Figure 19-11 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-pressure process. Heat is added and work is done in lifting the loaded piston. (b) The process on a p-V diagram. The work p ΔV is given by the shaded area.

$$\Delta E_{int} = Q - W$$

$$nC_V \Delta T = nC_D \Delta T - nR\Delta T$$

[A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, not on what type of process produces the change, $\Delta E_{int} = nC_V \Delta T$]

$$C_V n\Delta T = C_p n\Delta T - R n\Delta T$$

$$C_V = C_p - R$$
 [divide by $n\Delta T$]

$$C_p - C_V = R$$

This prediction of kinetic theory agrees well with experiment, not only for monatomic gases but also for gases in general, as long as their density is low enough so that we may treat them as ideal.

C_p is greater than C_v :

This C_p is greater than the molar specific heat at constant volume C_V , because energy must now be supplied not only to raise the temperature of the gas but also for the gas to do work as shown in Fig.

19-8 Degrees of freedom and molar specific heats: $E_{int} = (\frac{f}{2})nRT$ and $C_V = (\frac{f}{2})R$

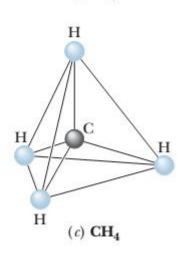
The prediction that agrees with experiment for monatomic gases but fails for diatomic and polyatomic gases.

Let us try to explain that molecules with more than one atom can store internal energy in forms other than translational kinetic energy.

Figure 19-13 shows common models of helium (a monatomic molecule, containing a single atom), oxygen (a diatomic molecule, containing two atoms), and methane (a polyatomic molecule).

James Clerk Maxwell introduced the theorem of the equipartition of energy:

Every kind of molecule has a certain number f of degrees of freedom (independent ways). Each degree of freedom can store energy of $\frac{1}{2}kT$ per molecule (or $\frac{1}{2}RT$ per mole). [f($\frac{1}{2}kT$) per molecule]



(a) He

Figure 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical

For the translational motion, superimpose an xyz coordinate system on any gas. The molecules will, in general, have velocity components along all three axes. Thus, gas molecules of all types have three degrees of translational freedom (three ways to move in translation) and, on average, an associated energy of $3(\frac{1}{2}kT)$ per molecule $[3(\frac{1}{2}RT)]$ per mole.

For the rotational motion, imagine the origin of our xyz coordinate system at the center of each molecule. In a gas, each molecule should be able to rotate with an angular velocity component along each of the three axes, so each gas should have three degrees of rotational freedom and, on average, an additional energy of $3(\frac{1}{2}kT)$ per molecule $[3(\frac{1}{2}RT)$ per mole].

However, experiment shows this is true only for the polyatomic molecules. According to quantum theory, the physics dealing with the allowed motions and energies of molecules and atoms, a monatomic gas molecule does not rotate and so has no rotational freedom $[0(\frac{1}{2}kT)=0]$ (a single atom cannot rotate like a top). A diatomic molecule can rotate like a top only about axes perpendicular to the line connecting the atoms and not about that line itself. Therefore, a diatomic molecule can have only two degrees of rotational freedom and a rotational energy of only $2(\frac{1}{2}kT)$ per molecule $[2(\frac{1}{2}RT)]$ per mole.

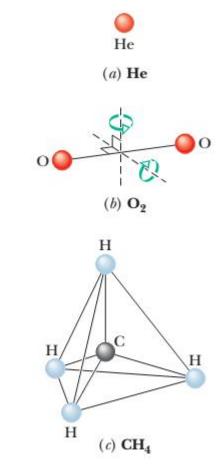


Figure 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical

To extend our analysis of molar specific heats to ideal diatomic and polyatomic gases, it is necessary to retrace the derivations of that analysis in detail. First, we replace $E_{int} = (3/2)$ nRT with $E_{int} = (f/2)$ nRT, where f is the number of degrees of freedom [Table 19-3]. Doing so leads to the prediction

$$C_V = (\frac{f}{2})R$$

This agrees for monatomic gases (f = 3). As Table 19-3 shows, this prediction also agrees with experiment for diatomic gases (f = 5), but it is too low for polyatomic gases (f = 6 for molecules comparable to CH_4).

Table 19-3 Degrees of Freedom for Various Molecules

		Degrees of Freedom			Predicted Molar Specific Heats	
Molecule	Example	Translational	Rotational	Total (f)	$C_V(\text{Eq. 19-51})$	$C_p = C_V + R$
Monatomic	Не	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O_2	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	$\mathrm{CH_4}$	3	3	6	3R	4R

Table 19-2 Molar Specific Heats at Constant Volume

Molecule	Examp	ole	C_V (J/mol·K)		
Monatomic	Ideal	3 2	R = 12.5		
	Real	He	12.5		
		Ar	12.6		
Diatomic	Ideal	$\frac{5}{2}R = 20.8$			
	Real	N_2	20.7		
		N_2 O_2	20.8		
Polyatomic	Ideal	3.	3R = 24.9		
	Real	NH ₄	29.0		
		CO_2	29.7		

Ammonium, NH4

47. The temperature of 2.00 mol of an ideal monatomic gas is raised 15.0 K at constant volume. What are (a) the work W done by the gas, (b) the energy transferred as heat Q, (c) the change ΔE_{int} in the internal energy of the gas, and (d) the change ΔK in the average kinetic energy per atom?

Solution:

Here, n = 2.00 mol

$$\Delta T = 15 \text{ K}$$

 $\Delta V = V - V = 0$
 $k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol-K}}{6.023 \times 10^{23}/\text{mol}} = 1.38 \times 10^{-23} \text{ J/K}$

(a)
$$W = p\Delta V = p(0) = 0$$

(b) Q =
$$nC_V\Delta T = n \left(\frac{3}{2}\right)R \Delta T = 2.00 \left(\frac{3}{2}\right)8.31 \left(15\right) = 373.95 \text{ J}$$

(c)
$$\Delta E_{int} = Q - W = 373.95 - 0 = 373.95 J$$

(d)
$$\Delta K = (\frac{3}{2})k\Delta T = (\frac{3}{2})(1.38 \times 10^{-23})15 = 31.05 \times 10^{-23} \text{ J}$$

$$[C_V = (\frac{3}{2})R]$$

 $[R = 8.31 \text{ J/mol} - \text{K}]$

48. When 20.9 J was added as heat to a particular ideal gas, the volume of the gas changed from 50.0 cm³ to 100 cm³ while the pressure remained at 1.00 atm. (a) By how much did the internal energy of the gas change? If the quantity of gas present was 2.00×10^{-3} mol, find (b) C_p and (c) C_V .

Solution:

Here, Q = +20.9 J

$$\Delta V = (100 - 50) \text{ cm}^3 = 50 \text{ cm}^3 = 50(10^{-2} \text{ m})^3 = 50 \text{x} 10^{-6} \text{ m}^3$$

$$p = 1.00 \text{ atm} = 1 \times 10^5 \text{ Pa}$$

$$n = 2.00 \times 10^{-3} \text{ mol}$$

(a)
$$\Delta E_{int} = Q - W = Q - p \Delta V = 20.9 - 1x10^{5}(50x10^{-6}) = 20.9 - 5.0 = 15.9 J$$

(b)
$$Q = nC_p\Delta T$$
 [p = constant]

$$C_p = \frac{Q}{n\Delta T}$$

Ideal gas law, pV = nRT

$$\frac{\Delta}{\Delta T}(pV) = \frac{\Delta}{\Delta T}(nRT)$$

$$p\frac{\Delta V}{\Delta T} = nR\frac{\Delta T}{\Delta T}$$

$$p\frac{\Delta V}{\Delta T} = nR$$

$$p\frac{\Delta V}{\Delta T} = nR$$

$$p\Delta V = nR \Delta T$$

$$\frac{p\Delta V}{R} = n \Delta T$$

$$C_{p} = \frac{Q}{\frac{p\Delta V}{R}}$$

$$C_{p} = \frac{QR}{p\Delta V} = \frac{20.9(8.31)}{1\times10^{5}(50\times10^{-6})} = \frac{173.68}{5.0} = 34.74 \text{ J/mol-K}$$

(c)
$$C_p - C_V = R$$

 $C_V = C_p - R = 34.74 - 8.31 = 26.43 \text{ J/mol-K}$

Sample Problem 19.07: Monatomic gas, heat, internal energy, and work

A bubble of 5.00 mol of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase ΔT of 20.0 °C at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal.

- (a) How much energy is added to the helium as heat during the increase and expansion?
- (b) What is the change ΔE_{int} in the internal energy of the helium during the temperature increase?
- (c) How much work W is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?