LECTURE 7 INTERNAL ENERGY AND SPECIFIC HEATS

Text Sections 20.8, 20.9, 20.11

Sample Problems 20.8, 20.9, 20.10

Suggested Questions 7, 9

Suggested Problems 81P

Summary Internal energy of an ideal gas
Molar specific heats of an ideal gas
Degrees of freedom
Equipartition of energy
Adiabatic expansion of an ideal gas

Specific objectives

• Explain what is meant by degrees of freedom for a molecule
• Calculate the average energy per molecule
• Apply the law \( c_p - c_v = R \)
• Explain and use the adiabatic ideal gas equation
Internal energy of an ideal gas

Consider a process where a small amount of heat is added to a gas system whose volume is kept constant (see Fig 20-8). During the process both the temperature and the pressure increase slightly.

The increase in internal energy of the system is given by the First Law:

\[ \Delta E_{\text{int}} = Q - W. \]

Since \( V \) is constant no work is done by the system, ie. \( W = 0 \) and \( \Delta E_{\text{int}} = Q \).

If there are \( n \) moles of gas in the system and the temperature increases from \( T \) to \( T + \Delta T \) in the process then

\[ Q = n c_V \Delta T \]

where \( c_V \) is the molar specific heat at constant volume of the gas. Therefore

\[ \Delta E_{\text{int}} = n c_V \Delta T \quad \text{constant \( V \) processes only all gases} \]

This equation is valid for all gases (including ideal gases). In general for real gases, \( c_V \) may vary and depend on both \( T \) and \( V \).

For ideal gases only, all equilibrium states on the same isotherm have the same internal energy.

Ideal gases have the property (no derivation here) that

\[ E_{\text{int}} = n c_V T \]

where \( c_V \) is constant and independent of both \( T \) and \( V \).

Therefore, for any process (whether or not it can be plotted as a curve on a \( p - V \) diagram) with initial state at temperature \( T \) and final state at \( T + \Delta T \),

\[ \Delta E_{\text{int}} = n c_V \Delta T \quad \text{any process ideal gases only} \]
(see Fig 20-9) Remember that this is not true for real gases except for constant V processes. (It is important to understand the conditions under which equations are valid!!)

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Molar specific heats at constant pressure for ideal gases

Now consider a process where a small amount of heat is added to an ideal gas system whose pressure is kept constant (see Fig 20-10). In this case

\[ Q = n c_p \Delta T \]

\[ W = p \Delta V = n R \Delta T \]

and \[ \Delta E_{\text{int}} = n c_v \Delta T \]

Since \[ \Delta E_{\text{int}} = Q - W \]

\[ n c_v \Delta T = n c_p \Delta T - n R \Delta T \]

or \[ c_p = c_v + R \]

This equation is true for all ideal gases.

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Molar specific heats, equipartition of energy and degrees of freedom

Measured values of \( c_v \) for real gases near ‘room’ temperature show interesting patterns (see Table 20-3).

For monatomic gases (those with 1 atom per molecule) such as He, Ne, Ar, Kr

\[ c_v \approx \frac{3}{2} R = 12.5 \text{ J.mol}^{-1}.\text{K}^{-1} \]

For diatomic gases (2 atoms per molecule) such as H\(_2\), N\(_2\), O\(_2\)

\[ c_v \approx \frac{5}{2} R = 20.8 \text{ J.mol}^{-1}.\text{K}^{-1} \]

For polyatomic gases (more than 2 atoms per molecule) such as CH\(_4\), NH\(_3\), CO\(_2\)

\[ c_v \geq 3R = 24.9 \text{ J.mol}^{-1}.\text{K}^{-1} \]
Why? A simple but non-rigorous explanation is provided by kinetic theory. The internal energy of an ideal gas is equal to the sum of the kinetic energies of its molecules.

For an ideal monatomic gas

$$E_{\text{int}} = n c_v T = n \frac{3}{2} R T = n \frac{3}{2} N_A k T$$

where \( k = R / N_A = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \) is called the Boltzmann constant.

Therefore

$$E_{\text{int}} = (n N_A) \left( \frac{3}{2} k T \right).$$

Since \( n N_A \) is the number of molecules in the system, \( 3 \times \frac{1}{2} k T \) is the average kinetic energy of a molecule.

**Equipartition of Energy Theorem**

Every kind of molecule has a certain number \( f \) of *degrees of freedom*, which are independent ways the molecule can store energy. On average each degree of freedom has associated with it an energy of \( \frac{1}{2} k T \) per molecule or \( \frac{1}{2} RT \) per mole.

Thus

$$E_{\text{int}} = (n N_A) f \left( \frac{1}{2} k T \right) = n f \left( \frac{1}{2} R T \right),$$

$$c_v = f \frac{1}{2} R \quad \text{and} \quad c_p = (f + 2) \frac{1}{2} R.$$

\( f = 3 \) for a monatomic gas. There are 3 independent directions in which a molecule may move, i.e. along the 3 coordinate axes.

\( f = 5 \) for a diatomic gas. In addition to the above 3 degrees of freedom a diatomic molecule has 2 rotational degrees of freedom. These correspond to rotation about 2 independent axes perpendicular to the line joining the 2 atoms (see Fig 20-11).

\( f = 6 \) for polyatomic gases. These molecules can also rotate about the axis perpendicular to the other two.

This simple classical picture works fairly well for monatomic gases, but gives values that are too low for many diatomic gases and for polyatomic gases. Much more accurate predictions are provided by quantum statistical mechanics developed during the 20C. This theory shows that \( c_v \) increases incrementally with temperature (see Fig 20-12). The classical picture works only in restricted temperature ranges.
Adiabatic expansion of an ideal gas

Consider a process in which an ideal gas system slowly expands and no heat is transferred to or from the system. This is an adiabatic process which can be plotted on a p – V diagram if the system always remains close to equilibrium states. The resulting curve is called an adiabat (see Fig 20-13).

It can be proved (not here) that for such a process

\[ p \, V^\gamma = \text{a constant} \]

where \( \gamma = \frac{c_p}{c_v} = 1 + \frac{R}{c_v} \)

is the ratio of specific heats, a number greater than 1.

Substitution for \( p \) from the Ideal Gas Law, \( p \, V = n \, R \, T \), gives the alternative equation

\[ T \, V^{\gamma - 1} = \text{a (different) constant} \]

Note that an adiabat is always steeper on a p – V diagram than the nearby isotherms since \( \gamma > 1 \).