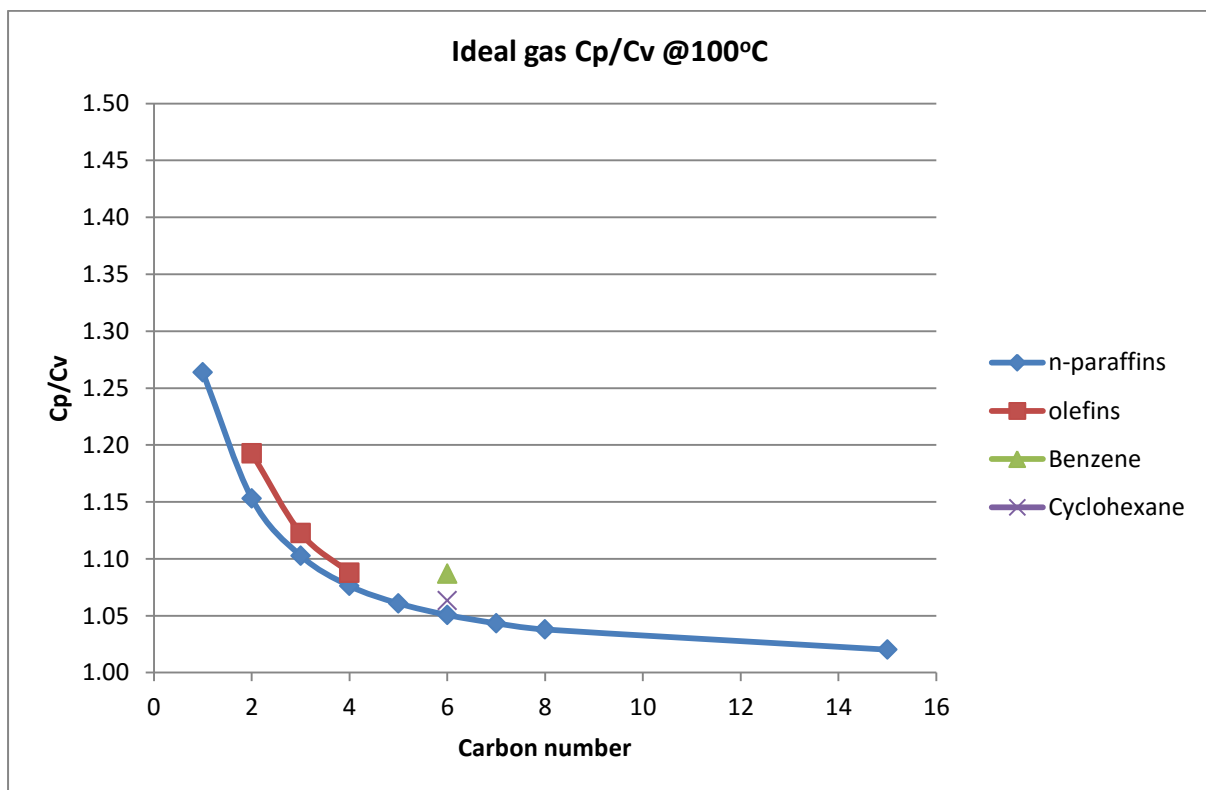




Understanding ideal gas ratio of specific heats (part 1)

Introduction

The ideal gas ratio of specific heats is used in the API 520 formulae for calculating pressure relief valve required area. For hydrocarbons, this ratio decreases as the molecular weight increases and it approaches 1 for large molecules. This is illustrated in the following chart (where C_p/C_v has been derived from C_p equations taken from Introduction to Chemical Engineering Thermodynamics by Smith and Van Ness).



The reason for the reduction in C_p/C_v with molecular weight is discussed below.

Discussion

C_v , the specific heat capacity at constant volume, is a measure of change of internal energy U with temperature (U is essentially the “molecular energy” usually denoted E in textbooks).

$$C_v = \frac{dU}{dT}$$

The specific heat at constant pressure, C_p , is equal to C_v plus PV work. For an ideal gas this is

$$C_p = C_v + R \quad (\text{where } R \text{ is the universal gas constant in consistent units.})$$

The molecular energy may be calculated from classical kinetic theory (although the results are not strictly correct since some energy absorption is not continuous - quantum physics applies!).

Molecular energy takes the following forms

1. Translational energy – from which the temperature is derived.
2. Rotational energy
3. Vibrational energy
4. Electronic energy - not important at “low” energy levels and will be neglected.
5. Nuclear energy - not important at “low” energy levels and will be neglected.

For an ideal gas the translational energy in a mole of gas (kinetic theory) is $3/2RT$ and the C_v contribution is therefore $3/2R$ (differentiate with respect to T).

For an ideal gas the rotational energy (general case) is calculated from the Principle of Equipartition of Energy. Since there are three degrees of freedom (three axes of rotation) then the energy is $3/2RT$ and the C_v contribution is therefore $3/2R$.

For an ideal diatomic gas there are 2 additional degrees of freedom for vibration which should result in an additional contribution of R to the C_v (see below). Polyatomic molecules have many vibrational modes.

Monatomic gases

The molecular energy is entirely translational. Rotational energy is negligible (the simple explanation is the small diameter of the molecule but it's not easily explained by classical theory).

$$C_v = 3/2R$$

$$C_p = 3/2R + R = 5/2R$$

$$C_p/C_v = 5/3 = 1.67$$

Diatomic gases

The molecular energy is comprised of (i) translational energy – $3/2R$ and (2) rotational energy – diatomic gases are linear, with small diameter on one axis therefore rotational energy is R not $3/2R$.

$$C_v = 3/2R + R = 5/2R \quad (\text{translational plus rotational})$$

$$C_p = 5/2R + R = 7/2R$$

$$C_p/C_v = 7/5 = 1.4$$

Note: in theory diatomic gases should have vibrational contribution of $2R$ giving $C_p/C_v = 1.3$. But vibrational energy for diatomic gases is negligible - kinetic and potential energy cancel for only two atoms?

Polyatomic gases

The molecular energy is comprised of (i) translational energy – $3/2R$ and (2) rotational energy - $3/2R$ plus (3) vibrational energy. This depends on the number of atoms (n) – classical theory indicates $3n-6$ degrees of freedom resulting in a contribution to C_v of $(3n-6)R/2$

Therefore for propane (11 atoms)

$$C_v = 3/2R + 3/2R + 27/2R = 33/2R$$

$$C_p = 33/2R + R = 35/2R$$

$$C_p/C_v = 35/33 = 1.06$$

For hexane (20 atoms)

$$C_v = 3/2R + 3/2R + 54/2R = 60/2R$$

$$C_p = 60/2R + R = 62/2R$$

$$C_p/C_v = 62/60 = 1.03$$

Conclusions

The mathematical reason why C_p/C_v decreases with increasing MW is that (1) C_v increases with MW and (2) there is a fixed difference between C_p and C_v . Therefore the ratio reduces.

The physical reason that C_v increases with increasing MW is that for a fixed amount of energy input, larger molecules take a bigger proportion in vibrational energy leaving less for translational energy which directly affects the temperature. Therefore the change of temperature for a given energy input is lower.

Note

There are many complications in the theory about rotational and vibrational modes. In fact C_p and C_v are not constants as indicated by the simple theory above but are temperature dependant. Specific heat increases with temperature so C_p/C_v reduces with temperature. Textbooks (e.g. Introduction to Chemical Engineering Thermodynamics – Smith & Van Ness) will give empirical equations for variation of “ideal gas” C_p with temperature.

