

Heat Capacity Ratios for Gases

Introduction

Chemistry is the study of matter, of the transformations that occur in matter and of the changes in *energy* (the ability to do work) that accompany those transformations. The potential for the absorption of or the release of energy by chemical systems, whether they be simple and inanimate or highly complex and living, is obviously of utmost importance in our confrontation with the natural world.

There are only a limited number of different ways in which energy can be added to or removed from a chemical system. Sometimes these are referred to as the ways in which energy can be *partitioned* within a chemical system. Most of these energies are *quantized* in that the molecule has available to it only certain energy levels or states in which it can exist. It may be raised from one allowed quantum state to a higher less stable quantum state or the reverse relaxation from a higher state to a lower quantum state may occur. But only these allowed transitions may occur.

The different ways a chemical system can contain energy are, in order of decreasing spacing of the quantized levels:

- i. Nuclear energy
- ii. Electronic binding energy
- iii. Vibrational energies
- iv. Rotational energies
- v. Translational energies
- vi. Intramolecular interactions
- vii. Electron spin (ESR)
- viii. Nuclear spin (NMR)

This experiment involves the measurement of the *heat capacity* of some simple gaseous systems. Heat capacity is a measure of the ability of a chemical system to absorb energy or heat for a given increase in temperature. A substance with a large heat capacity, *e.g.*, water, can absorb a lot of heat with only a very small simultaneous increase in temperature, the result (to a large extent) of strong hydrogen bonding. In practical terms, heat capacity is of great importance in such widely different things as the weather, cooking, home construction, and maintaining body temperature.

An atom or molecule must have a total of $3N$ degrees of motional freedom, where N is the number of atoms.¹ There are 3 degrees of translational freedom along the x , y , and z directions. A linear molecule possesses two rotational degrees of freedom and $3N - 5$ degrees of vibrational degrees of freedom. A nonlinear molecule possesses three rotational degrees of freedom and $3N - 6$ vibrational degrees of freedom. From classical statistical mechanics, the theorem of the equipartition of energy states that the total energy of the system is equally partitioned among all the degrees of freedom. For a mole of an ideal gas, each translational and rotational degree of freedom possesses energy $RT/2$, whereas each vibrational degree of freedom possesses energy RT , where R is 8.314 J/mol K and T is the absolute temperature. This is so because the vibrational energy contains two terms, one kinetic ($RT/2$) and one potential ($RT/2$).

The heat capacity of a gaseous system can be specified for a change in energy at constant volume or at constant pressure. From the first law

$$dU = \delta q + \delta w \quad (1)$$

If there is no change in the volume, V , then no pressure-volume work will be done so that

$$dU = \delta q_v \quad (2)$$

We define the heat capacity at constant-volume as

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad (3)$$

If there is a change in volume, V , then pressure-volume work will be done during the absorption of energy. Assuming one mole of an ideal gas, the second term in (1) becomes $P\Delta V$ so that

$$\delta q_p = dU + PdV = dH$$

and the heat capacity at constant-pressure is given by

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (4)$$

Since $H = U + PV = U + RT$ (for one mole of an ideal gas), we can write

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + R \quad (5)$$

or

$$C_p = C_v + R \quad (6)$$

In summary, we have three contributions to the energy

$$U = E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} \quad (7)$$

where

$$E_{\text{vib}} = \begin{cases} (3N-6)RT & \text{for nonlinear molecules} \\ (3N-5)RT & \text{for linear molecules} \\ 0 & \text{for monatomic gases} \end{cases} \quad (8a)$$

$$E_{\text{rot}} = \begin{cases} 3(RT/2) & \text{for nonlinear molecules} \\ 2(RT/2) & \text{for linear molecules} \\ 0 & \text{for monatomic gases} \end{cases} \quad (8b)$$

where N is the number of atoms in the molecule. And for all gases

$$E_{\text{trans}} = 3(RT/2) \quad (8c)$$

For example, for the ammonia molecule, NH_3 , we have

$$U = 6RT + 3RT/2 + 3RT/2 = 9RT \quad (9)$$

The molar heat capacity C_v would be

$$\begin{aligned} C_v &= (\partial U / \partial T)_v = 9R \\ &= 74.8 \text{ J/K mol} \end{aligned} \quad (10)$$

In fact, observed heat capacities tend to be considerably less than those values calculated on the basis of translational, rotational and vibrational energy levels. While excitation of the molecule's translational and rotational energies is possible at normal temperatures, the first excited vibrational level for most molecules lies too far above the vibrational ground state to be excited at the ambient temperature. Therefore, in the case of ammonia, the contribution of $6R$ from the vibrational energy excitation is unreasonable. Only at very high temperatures (ca. 3000 K), does vibrational excitations from thermal energy begin to make a significant contribution to the heat capacity.

*"When sound travels through a gas, the particles of the medium move back and forth in the direction of the wave propagation and form what is known as a longitudinal pressure (or compression) wave. (At high frequency) the time interval between the passage of a compression maximum and minimum at a particular point is very brief, of the order of a few nanoseconds. We can therefore assume that the pressure variation occurs rapidly enough for heat conduction to be negligible, that is, the compression and expansion in the sound wave are nearly adiabatic (no heat transfer) processes."*²

Adiabatic changes in ideal gases obey the expression

$$PV^\gamma = \text{constant} \quad (11)$$

where

$$\gamma = C_p/C_v \quad (12)$$

The heat capacity ratio, γ , of a gas can be determined by measuring the speed of sound, c :

$$\gamma = Mc^2/RT \quad (13)$$

where M is the molecular weight of the gas in kg/mole, c is in meters/second, R is 8.314 J/mol K and T is the absolute temperature. Therefore, from Eqs.(6)-(12) and a value of γ , we can calculate C_v and C_p .

Procedure

The procedure given in Reference 1 will be followed with slight variations described by the instructor.

1. You will study argon (Ar), nitrogen (N₂) and carbon dioxide (CO₂). You will get cleaner signals if you stay at and above 1300 Hz.
2. Measure five node positions (to 0.1 mm) with the oscilloscope for each gas at one frequency. Start with the piston largely out of the cylinder and move it towards the microphone to minimize pulling air into the cylinder. The distance between nodes is $\lambda/2$ where λ is the wavelength. Then change the frequency by about twenty percent and again measure five node positions for each of the three gases.
3. Remember to record the ambient temperature, noting the possible error, ΔT , in reading the thermometer, and be sure to reduce the gas flow rate to a very low value such that the pressure inside the tube equals ambient pressure.
4. Damage to the phosphorescent screen on the oscilloscope may occur if a bright spot is allowed to persist for more than a few seconds.

Calculations

For each gas calculate the average wavelength, λ , and a standard deviation on λ for the four values at each frequency.

Use the relationship

$$c = \lambda f \quad (14)$$

to calculate the speed of sound, c , at each frequency, f , for each gas. Calculate the average value of c for each gas. Use the larger of the two standard deviations for the two λ values to calculate an estimated error in c from

$$(\partial c / \partial \lambda) = f \quad (15)$$

$$\Delta c = (\partial c / \partial \lambda) \Delta \lambda \quad (16)$$

$$= f \Delta \lambda \quad (17)$$

where your standard deviation on λ will be used for $\Delta \lambda$ in equation (17). Calculate Δc for each gas.

The heat capacity ratio, γ , will be calculated from equation (13). Estimate an error $\Delta \gamma$, in γ from

$$\Delta \gamma = \left| \left(\frac{\partial \gamma}{\partial c} \right)_T \right| \Delta c + \left| \left(\frac{\partial \gamma}{\partial T} \right)_c \right| \Delta T \quad (18)$$

$$= (2Mc/RT) \Delta c + (Mc^2/RT^2) \Delta T \quad (19)$$

using your values of c , Δc , T , and ΔT . Errors in M can be assumed negligible.

For the three gases, calculate from the equipartition theorem and equations (3), (6) and (12) the theoretical values of C_v , C_p and γ , assuming contributions from translational, rotational and vibrational energies. Repeat the calculations for N_2 and CO_2 without the vibrational energy contribution. Note that as the vibrational contribution is eliminated, γ increases. Do your observed values of γ suggest that the vibrational contribution is important in the two molecular gases? Can you justify the differences in this contribution for the two gases?

Report

Give your calculations for your observed values of γ for all three gases, with an estimate of uncertainty, $\Delta \gamma$. Compare your values with the values calculated from the equipartition theorem (with and without vibrational contributions) and with the literature values.^{3,4}

References

1. D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 5th Edition (McGraw-Hill, New York, 1989) pp. 104-107, 113-118. In the 6th edition, pp. 105-107, 112-116. Any edition is acceptable.
2. G. Peter Matthews, *Experimental Physical Chemistry* (Clarendon Press, Oxford, 1985) pp. 235-237.
3. S. O. Colgate, K. R. Williams, K. Reed, C. A. Hart, *J. Chem. Ed.*, **64**, 553 (1987).
4. P. W. Atkins, *Physical Chemistry*, 5th Edition, (W.H. Freeman and Company, New York, 1994) p.C9, Table 2.12; or 6th edition, 1998, p.923, Table 2.6; or 7th edition, 2002, p.1076, Table 2.6.

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