

The curve in Figure 16.11 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 16.12 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode  $T \gg \theta_M$ ) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute  $\frac{3}{2}R$  to the molar heat capacity. If we denote the number of active rotational modes by  $\nu_R^\ddagger$  (so for most molecules at normal temperatures  $\nu_R^\ddagger = 2$  for linear molecules, and 3 for non-linear molecules), then

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \dots$$

The equipartition value  $C_{V,m} = 2.5R$  is reached when all the degrees of freedom are active. For a diatomic molecule,  $\nu_R^\ddagger = 2$  and  $C_{V,m} = 2.5R$  is reached when the vibrational modes are also active. For a non-linear molecule,  $\nu_R^\ddagger = 3$  and  $C_{V,m} = 2.5R$  is reached when the vibrational modes are also active. The vibrational modes are active when  $T \gg \theta_M$ . The vibrational temperature  $\theta_M$  is defined as  $\theta_M = \frac{h\nu}{k_B}$ . For a diatomic molecule,  $\theta_M = \frac{h\nu}{k_B} = \frac{h}{k_B} \nu = \frac{6.626 \times 10^{-34} \text{ J s}}{1.381 \times 10^{-23} \text{ J K}^{-1}} \nu = 4.79 \times 10^{-11} \nu$ . For a non-linear molecule,  $\theta_M = \frac{h\nu}{k_B} = \frac{h}{k_B} \nu = \frac{6.626 \times 10^{-34} \text{ J s}}{1.381 \times 10^{-23} \text{ J K}^{-1}} \nu = 4.79 \times 10^{-11} \nu$ .

### Solutions to exercises

**16.1** The vibrational energy is given by  $\epsilon = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right)$ . The vibrational energy is  $\epsilon = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right)$ .

$$\epsilon = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right)$$

where  $n = 0, 1, 2, \dots$  is the vibrational quantum number.

$$\epsilon = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right) = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right)$$

**16.2** The vibrational energy is

$$\epsilon = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right) = \frac{1}{2}h\nu + h\nu \left( \frac{1}{2} + n \right)$$

**16.3**  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \dots$

where  $\nu_R^\ddagger = 2$  for linear molecules,

# Physical Chemistry 9th Edition Solutions

**Y Pai**

A decorative graphic element consisting of a light blue horizontal bar with a rounded right end, and a red semi-circular shape behind it.

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**The Journal of Physical Chemistry** Wilder Dwight Bancroft, 1917 Includes section New Books

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**The Encyclopaedia Britannica**, 1929 *Encyclopaedia Britannica*, 1929 The Encyclopedia Britannica James Louis Garvin, Franklin Henry Hooper, Warren E. Cox, 1929 *Physical Chemistry for Schools* Henry John Horstman Fenton, 1916

**Chemical Engineering Catalog**, 1918 Bulletin of the Chemical Society of Japan Nihon Kagakkai, 1986

**Industrial & Engineering Chemistry**, 1923 **The United States Catalog** Mary Burnham, Carol Hurd, 1928

**The Journal of Industrial and Engineering Chemistry**, 1923 **Laboratory Manual of Organic Chemistry** Harry Linn Fisher, 1924

**Treatise on Thermodynamics, Based on the Methods of Gibbs and De Donder, I. Prigogine and R. Defay: Chemical thermodynamics. 1. Thermodynamics, 2. Thermochemistry** Ilya Prigogine, Raymond Defay, 1962

*The Lancet*, 1927 The Chemical News : and Journal of Physical Science, 1908

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