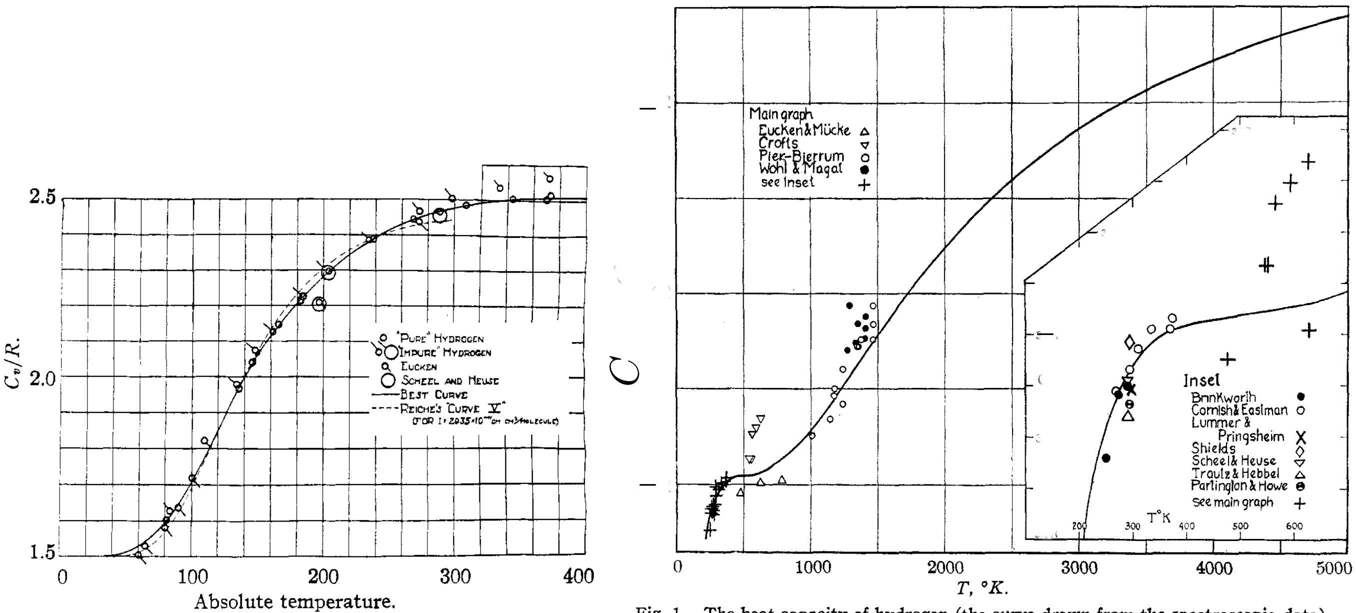


Fig. 3.—Specific heat of hydrogen.

Cornish and Eastman (1928)

Fig. 1.—The heat capacity of hydrogen (the curve drawn from the spectroscopic data).

Davis and Johnston (1934)

Figure 1: Experimental heat capacity data for H$_2$.

The heat capacity at fixed volume (experimental data plotted above) is given by

$$C_V = \frac{dU}{dT} \tag{1}$$

In many quantum mechanical systems (including a H$_2$ molecule) energy cannot vary continuously. There is a discrete set of allowed energies for each degree of freedom associated with the gas molecule.

1. Translational K.E. in one direction: $\{1 \times 10^{-39}\ \text{J}, 4 \times 10^{-39}\ \text{J}, 9 \times 10^{-39}\ \text{J}, \ldots\}$
2. Rotational K.E.: $\{0, 4 \times 10^{-21}\ \text{J}, 4 \times 10^{-21}\ \text{J}, 4 \times 10^{-21}\ \text{J}, 12 \times 10^{-21}\ \text{J}, \ldots\}$
3. Vibrational energy: $\left\{ \underbrace{4.4 \times 10^{-20}\ \text{J}}_{\text{“zero point energy”}}, 13.2 \times 10^{-20}\ \text{J}, 22 \times 10^{-20}\ \text{J}, \ldots \right\}$

If the temperature is small ($\frac{1}{2}k_BT$ is small), there can arise a conflict between the rules of quantum mechanics and the equipartition theorem.

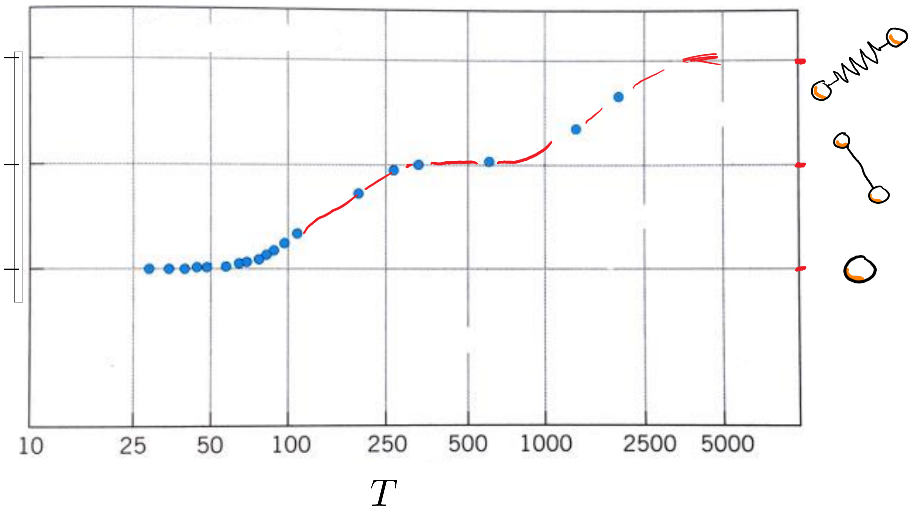
For a diatomic molecule, we can write its classical energy in terms of independent coordinates as:

$$E = \underbrace{\frac{1}{2}(2m)v_x^2 + \frac{1}{2}(2m)v_y^2 + \frac{1}{2}(2m)v_z^2}_{\text{Translational K.E. of entire molecule}} + \underbrace{\frac{1}{2}\frac{L_x^2}{I_x} + \frac{1}{2}\frac{L_y^2}{I_y}}_{\text{Rotational K.E.}} + \underbrace{\frac{1}{2}m\left(\frac{1}{2}\frac{d\ell}{dt}\right)^2 + \frac{1}{2}k(\ell - \ell_0)^2}_{\text{K.E. + P.E. of spring}} \tag{2}$$

This should (according to the equipartition theorem) give us

$$\begin{array}{rcl} E & = & \underbrace{\begin{array}{ccccc} \frac{1}{2}(2m)v_x^2 & + & \frac{1}{2}(2m)v_y^2 & + & \frac{1}{2}(2m)v_z^2 \\ \frac{1}{2}k_BT & + & \frac{1}{2}k_BT & + & \frac{1}{2}k_BT \end{array}}_{\text{Translational K.E. of entire molecule}} + \underbrace{\begin{array}{ccc} \frac{1}{2}\frac{L_x^2}{I_x} & + & \frac{1}{2}\frac{L_y^2}{I_y} \\ \frac{1}{2}k_BT & + & \frac{1}{2}k_BT \end{array}}_{\text{Rotational K.E.}} + \underbrace{\begin{array}{ccc} \frac{1}{2}m\left(\frac{1}{2}\frac{d\ell}{dt}\right)^2 & + & \frac{1}{2}k(\ell-\ell_0)^2 \\ \frac{1}{2}k_BT & + & \frac{1}{2}k_BT \end{array}}_{\text{K.E. + P.E. of spring}} \\ U(T) & = & \end{array} \tag{3}$$

But now we can see that if $\frac{1}{2}k_BT < 0.1 \times 10^{-20}$ J then the vibrational state of the H_2 molecule cannot respond to changes in temperature. The molecule remains stuck in its lowest energy state. Its behavior is equivalent to a molecule connected by a rigid rod.



Highest temperatures In excess of 5000 K, the molecule behaves like we would expect a springy diatomic molecule to do classically. This is because

$$\frac{1}{2}k_BT \gg 8.8 \times 10^{-20} \text{ J} \tag{4}$$

which is the amount of energy required to "excite" a hydrogen molecule's vibrational degrees of freedom.

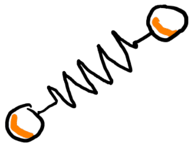


Figure 2: $f = 7$

Lowest temperatures At very low temperatures, less than around 50 K, the hydrogen molecule behaves as if it were a monatomic atom, since there isn't even enough energy available to rotate it. In terms of math

$$\frac{1}{2}k_BT \ll 4 \times 10^{-21} \text{ J}. \tag{5}$$

Figure 3: $f = 3$

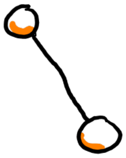


Figure 4: $f = 5$

Middle temperatures Around 500 K, we have a Goldilocks range of temperatures (not too hot, and not too cold) where the hydrogen molecule will behave like a rigid rod: it's got enough energy to rotate, but not enough energy to vibrate.

$$4 \times 10^{-21} \text{ J} \ll \frac{1}{2} k_B T \ll 8.8 \times 10^{-20} \text{ J}. \tag{6}$$