Molecular Thermodynamics
Week 1 Lecture Assessments
Energy Unit Conversions

December 11, 2013

`Thermovid_01_03`

A) Determine the energy, E, of a photon with a wavelength of 400 nm expressed in joules and in wavenumber units.

    (a) 7.495×10^{-1} joules; 25,000 cm^{-1}

    (b) 7.495×10^{-20} joules; 25,000 cm^{-1}

    (c) 4.966×10^{-19} joules 12,500 cm^{-1}

    (d) $\boxed{4.966 \times 10^{-19} \text{ joules; 25,000 cm}^{-1}}$

    (e) 4.966×10^{-17} joules; 25,000 cm^{-1}

    (f) 4.966×10^{-17} joules; 50,000 s^{-1}

Answers:
A review from general chemistry: Electromagnetic energy is carried by discrete bundles of energy called photons. The energy, E, of a photon is given by

$$E = h\nu \tag{1}$$

where ν is the frequency of light and h is Planck's constant (6.6261×10^{-34} J·s). The relationship between the speed of light, c, the frequency, ν, and the wavelength of the light, λ is

$$c = \nu\lambda. \tag{2}$$

Combining (1) and (2), you can verify that

$$E = \frac{hc}{\lambda} \tag{3}$$

Equation (3) tells us that the energy of electromagnetic radiation is *inversely* proportional to its wavelength, λ. A quantity known as the wavenumber, $\tilde{\nu}$, is defined as $\tilde{\nu} = 1/\lambda$ such that

$$E = hc\tilde{\nu}. \tag{4}$$

Energy in wavenumbers is frequently expressed in cm^{-1} (*inverse* cm).

Therefore, to calculate the frequency, in Hertz, s^{-1}, we can directly convert from wavelength to frequency using (2), thus:

$$\nu = \frac{c}{\lambda} = \frac{1}{400 \text{ nm}}\left(\frac{10^9 \text{ nm}}{1 \text{ m}}\right)\left(\frac{2.998 \times 10^8 \text{ m}}{\text{s}}\right) = 7.495 \times 10^{14} \text{ s}^{-1}$$

Now we can use (1) to convert to joules:

$$E = h\nu = 6.626 \times 10^{-34}\,\text{J} \cdot \text{s}\left(\frac{7.495 \times 10^{14}}{\text{s}}\right) = 4.966 \times 10^{-19}\,\text{J}$$

To convert to wavenumbers, we can simple convert nanometers to centimeters and take the inverse of the number:

$$400\ \text{nm}\left(\frac{10^{-7}\text{cm}}{\text{nm}}\right) = 4 \times 10^{-5}\ \text{cm}$$

and therefore,

$$\bar{\nu} = \frac{1}{4 \times 10^{-5}\ \text{cm}} = 25,000\ \text{cm}^{-1}$$

Molecular Thermodynamics
Week 1 Lecture Assessments
Energy Unit Conversions

December 11, 2013

`Thermovid_01_04`

A) Another common method chemists use to quantify energy is to express the amount of energy needed to break one mole of chemical bonds of any particular type. This quantity is frequently expressed in kJ/mol (kilojoules/mole), or sometimes kcal/mol (kilocalories/mole - recall that there are 4.184 joules/calorie).

In this lecture, you learned that it takes $246\,\text{kJ/mol}$ of energy to initiate the reaction of $Cl_2 + H_2 \longrightarrow 2\,HCl$. Determine the wavelength of a photon (in nm) having the minimum energy needed to break one Cl_2 bond.

   (a) 450.1 nm

   (b) $\boxed{486.3\ \text{nm}}$

   (c) 486.3×10^{-9} nm

   (d) 450.1×10^{-9} nm

   (e) 408.5 nm

   (f) 4.085 nm

<u>Answer:</u>

We can convert from kJ/mol to kJ/bond Cl_2 broken by dividing by Avogadro's number.

$$\frac{246 \text{ kJ/mol}}{6.022 \times 10^{23} \text{ bonds/mol}} \left(\frac{10^3 \text{J}}{\text{kJ}} \right) = 4.085 \times 10^{-19} \text{ J/bond}$$

We can then rearrange and solve for the wavelength, λ:

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.998 \times 10^8 \text{ m/s}}{4.085 \times 10^{-19} \text{ J}} = 4.863 \times 10^{-7} \text{ m} = 486.3 \text{ nm}$$

Molecular Thermodynamics
Week 1 Lecture Assessments
Energy Unit Conversions

December 11, 2013

`Thermovid_01_05`

A) Use the equation for the quantized energy levels of a hydrogen atom,

$$\epsilon_n = -\frac{2.17869 \times 10^{-18}}{n^2} \text{J},$$

to calculate the energy required to ionize a hydrogen atom in its ground electronic state. *Hint*: To ionize a molecule means to remove an electron to infinite distance. Give your answer in kJ/mol and eV. An electron-volt is another common unit of energy, and it is often used when discussing electronic energy levels (1 eV = 1.602 $\times 10^{-19}$ J = 8066 cm^{-1}).

 (a) 1.312 kJ $\cdot$ mol^{-1} and 13.6 eV

 (b) $\boxed{1312 \text{ kJ} \cdot \text{mol}^{-1} \text{ and } 13.6 \text{ eV}}$

 (c) 5489.4 kJ $\cdot$ mol^{-1} and 13.6 eV

 (d) 1312 kJ $\cdot$ mol^{-1} and 3.491 $\times 10^{-36}$ eV

 (e) 2.179 $\times 10^{-19}$ kJ $\cdot$ mol^{-1} and 13.6 eV

 (f) 2.179 $\times 10^{-19}$ kJ $\cdot$ mol^{-1} and 1.90 $\times 10^{25}$ eV

<u>Answer:</u>

To ionize hydrogen starting from the ground state ($n = 1$) we want to completely separate the electron from the proton, which is the limit as n gets infinitely large. So, the final ionized state will have the energy associated with $n = \infty$. Note that this is what we define as the zero of energy when considering this system, and zero is what you get as the denominator goes to ∞. To get the energy of ionization, take the difference between the final ($n = \infty$, ionized) and initial ($n = 1$, ground) states,

$$\varepsilon_{\text{ionization}} = -\frac{2.17869 \times 10^{-18} \text{ J}}{\infty^2} - \left(-\frac{2.17869 \times 10^{-18} \text{ J}}{1^2}\right) = 2.17869 \times 10^{-18} \text{ J}$$

This is in joules per atom, so now multiply by Avogadro's number to convert to the molar value, and convert to kilojoules,

$$\varepsilon_{\text{ionization}} = \left(2.17869 \times 10^{-18} \text{ J}\right)\left(6.022 \times 10^{23} \text{ mol}^{-1}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right)$$

$$\boxed{\varepsilon_{\text{ionization}} = 1312 \text{ kJ} \cdot \text{mol}^{-1}}$$

Starting with the original value in joules, convert to eV using the following unit conversion,

$$\varepsilon_{\text{ionization}} = \left(2.17869 \times 10^{-18} \text{ J}\right) \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right) = \boxed{13.6 \text{ eV}}$$

and note that the value in eV is per atom.

B) What are two ways to distribute energy in an atom?

    (a) rotational and translational

    (b) $\boxed{\text{translational and electronic}}$

    (c) translational and vibrational

    (d) vibrational and electronic

    (e) electronic and rotational

Answer:

An atom can move through space and thus has translational energy. The electrons in the atom also have some energy associated with the electronic state. As you will see in future lectures, a molecule can additionally store energy in vibrations and rotations.

C) For a hydrogen atom in a 1-dimensional box that is 1 nm (nanometer) in length, what is the energy difference between the ground state $n = 1$ and the first excited state $n = 2$? The mass of a hydrogen atom is 1.674×10^{-27} kg.

    (a) 1.321×10^{-22} J

    (b) 2.728×10^{-23} J

    (c) 3.303×10^{-33} J

    (d) 2.643×10^{-22} J

    (e) $\boxed{9.835 \times 10^{-23} \text{ J}}$

Answer:

Translational energy levels are determined with the equation,

$$\epsilon_{\text{trans}} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

where a, b, and c are the dimensions of a macroscopic box.

In one dimension,

$$\epsilon_{\text{trans}} = \frac{h^2}{8m} \left(\frac{n^2}{a^2}\right),$$

and if we wish to find the difference between the first and second energy levels,

$$\epsilon_{\text{trans}} = \frac{h^2}{8ma^2} \left(2^2 - 1^2\right).$$

Inserting the numbers,

$$\epsilon_{\text{trans}} = \left(\frac{(6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}^2} \cdot \text{s})^2}{8 \cdot 1.674 \times 10^{-27} \text{ kg} \cdot (10^{-9} \text{ m})^2}\right) \left(2^2 - 1^2\right) = 9.835 \times 10^{-23} \text{ J}.$$

Recall that one joule is equivalent to one kg m^2/s^2.

Molecular Thermodynamics
Week 1 Lecture Assessments
Energy Unit Conversions

May 20, 2013

`Thermovid_01_06`

A) In the lecture slides, the moment of inertia was defined as,

$$I = m_1 R_1^2 + m_2 R_2^2.$$

It will be shown in the solution to this problem that the moment of inertia can be written,

$$I = \mu R_e^2 \tag{1}$$

where R_e is the equilibrium bond length (i.e., the sum of the magnitudes of R_1 and R_2), and μ is the reduced mass,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

Use the equation

$$I = \mu R_e^2 \tag{2}$$

and the formula for the $J = 1$ energy level for a diatomic molecule that was just presented, to calculate the $J = 1$ rotational energy level for $^1\text{H}^{79}\text{Br}$. The atomic mass of ^{79}Br is 78.918 amu and the equilibrium bond length is 142.0 pm. The atomic mass of ^1H is 1.008 amu.

(a) $\boxed{3.336 \times 10^{-22} \text{ J}}$

(b) 3.336×10^{-19} J

(c) 3.333×10^{-47} J

(d) 1.653×10^{-47} J

(e) 6.022×10^{-34} J

Answer:

If we set up a one dimensional coordinate system where zero is at the center of mass, then

$$m_1 R_1 + m_2 R_2 = 0, \tag{3}$$

solving for R_1 and R_2 we obtain,

$$R_1 = -R_2 \frac{m_2}{m_1} \tag{4}$$

$$R_2 = -R_1 \frac{m_1}{m_2} \tag{5}$$

Also, in keeping with our sign convention,

$$-R_1 + R_2 = R_e,$$

and therefore

$$R_1 = R_2 - R_e \tag{6}$$
$$R_2 = R_e + R_1. \tag{7}$$

Now we can substitute (5) and (6) into (3) and (4) respectively, and do some rearrangement to obtain,

$$R_1 + R_1 \frac{m_1}{m_2} = -R_e \tag{8}$$

and,

$$R_2 + R_2 \frac{m_2}{m_1} = R_e. \tag{9}$$

After some further rearrangement,

$$R_1 \left(\frac{m_2 + m_1}{m_2} \right) = -R_e$$

and,

$$R_2 \left(\frac{m_1 + m_2}{m_1} \right) = R_e.$$

Solving for each of the radii R_1 and R_2,

$$R_1 = - \left(\frac{m_2}{m_1 + m_2} \right) R_e \tag{10}$$

and,

$$R_2 = \left(\frac{m_1}{m_1 + m_2} \right) R_e. \tag{11}$$

We can now use the definition of the moment of inertia and substitute in the values for R_1 and R_2 from Equations (9) and (10) to obtain.

$$I = m_1 R_1^2 + m_2 R_2^2 = m_1 \left(- \left(\frac{m_2}{m_1 + m_2} \right) R_e \right)^2 + m_2 \left(\left(\frac{m_1}{m_1 + m_2} \right) R_e \right)^2 = \frac{m_1 m_2}{(m_1 + m_2)} R_e^2 = \mu R e^2$$

Now we can calculate the moment of inertia for HBr,

$$\mu = \left(\frac{1.008 \text{ amu} \times \ 78.918 \text{ amu}}{1.008 \text{ amu} + 78.918 \ \text{ amu}} \right) \times 1.661 \times 10^{-27} \frac{\text{kg}}{\text{amu}}$$
$$= 1.653 \times 10^{-27} \text{ kg}$$

and therefore,

$$I = \mu R_e^2 = 1.653 \times 10^{-27} \text{ kg} \times (142.0 \times 10^{-12})^2 \text{m}^2 = 3.333 \times 10^{-47} \text{kg m}^2.$$

2

The $J = 1$ energy level for a diatomic molecule (approximated as a ridgid rotor) can be found on the *Rotational Energy Levels* slide. The formula is,

$$\epsilon_{j=1} = \frac{\hbar^2}{I},$$

therefore,

$$\epsilon_{j=1} = \frac{(1.0546 \times 10^{-34}\,\text{J} \cdot \text{s})^2}{3.333 \times 10^{-47}\ \text{kg m}^2} = 3.336 \times 10^{-22}\,\text{J}.$$

Molecular Thermodynamics
Week 1 Lecture Assessments
Energy Unit Conversions

May 20, 2013

`Thermovid_01_07`

A) Determine the number of vibrational degrees of freedom of methane (CH_4):

    (a) 15

    (b) $\boxed{9}$

    (c) 3

    (d) 10

    (e) 5

    (f) 6

    (g) 4

    (h) 7

Answer:

Start from the fact that the total number of degrees of freedom must be 3 times the total number of atoms ($3N$), since each atom can move in 3D space. From there we break it up into different categories. There are always 3 translational degrees of freedom (the whole molecule moving in 3D space). For rotations, the only question is linear or nonlinear. For a linear molecule there are 2 rotations, and for a nonlinear molecule there are 3 rotations. In this case there are 3 because the molecule is nonlinear. The vibrations are whatever is left from the total (total minus translations minus rotations). For a linear molecule there are $3N - 5$ vibrations, and for a nonlinear molecule there are $3N - 6$ vibrations.

Methane has a total of 5 atoms, and is nonlinear. Thus we can fill in the table below as follows:

molecule	N	total ($3N$)	translations	rotations	vibrations
CH_4	5	15	3	3	9

`Thermovid_01_07`

B) Determine the number of vibrational degrees of freedom of carbon disulfide (CS_2):

    (a) 1

    (b) 3

    (c) 5

    (d) 9

    (e) 2

    (f) $\boxed{4}$

(g) 7

(h) 6

<u>Answer:</u>

Start from the fact that the total number of degrees of freedom must be 3 times the total number of atoms ($3N$), since each atom can move in 3D space. From there we break it up into different categories. There are always 3 translational degrees of freedom (the whole molecule moving in 3D space). For rotations, the only question is linear or nonlinear. For a linear molecule there are 2 rotations, and for a nonlinear molecule there are 3 rotations. In this case there are 2 because the molecule is linear. The vibrations are whatever is left from the total (total minus translations minus rotations). For a linear molecule there are $3N - 5$ vibrations, and for a nonlinear molecule there are $3N - 6$ vibrations.

Carbon disulfide has a total of 3 atoms, and is linear. Thus we can fill in the table below as follows:

molecule	N	total ($3N$)	translations	rotations	vibrations
CS_2	3	9	3	2	4

2

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_01`

A) Given what you now know about *intensive* and *extensive* properties of a system, rationalize whether

    (a) Viscosity $\boxed{Intensive}$

    (b) Molar Volume $\boxed{Intensive}$

    (c) Energy $\boxed{Extensive}$

are *intensive* or *extensive* system properties.

Answer:
Recall that if a property is *intensive*, then the property is independent of the amount of substance present in the physical system that is being described by the property. Thus, viscosity is an *intensive* property - you could measure the viscosity of a 1 mL or 5 mL sample of a substance, for example, and get the same result. Molar volume must be *intensive* as well, it is a volume that always references the same amount of substance, namely, one mole. Volume by itself, however, is an *extensive* quantity - volume depends on the amount of substance present. We can always divide an *extensive* property (like Volume), by an *extensive* property (like an exact amount, such as the number of moles) to get an *intensive* quantity such as, in this case, molar volume. Energy is an *extensive* property - we need to know how much of a substance is present in a system we are attempting to describe in order to quantify the energy. For example, it wouldn't make any sense to ask:"What is the energy of methane gas?" We would have to know how much methane gas we were talking about to assign a value to this.

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_02`

A) *True* or $\boxed{\textit{False}}$: The compressibility of methane gas at very low temperature is greater than an ideal gas.

Answer
The answer is false. Look at the second lecture slide in the *Non-ideal gas equation of state* video. There you see that the compressibility factor, Z, is less than one. Attractive forces dominate the intermolecular potential, and therefore $\bar{V}_{Real} < \bar{V}_{Ideal}$ (think of it as if the molecules are pulling closer to one another which shrinks the volume relative to that of an ideal gas with the same number of molecules).

B) As the temperature of a gas is increased at constant volume the compressibility factor will ($\boxed{\textit{increase}}$ or *decrease*) and ($\boxed{\textit{repulsion}}$ or *attraction*) will dominate the intermolecular interactions.

Answer:

Look at the second lecture slide in the *Non-ideal gas equation of state* video. There you see that the compressibility factor, Z, becomes greater than unity as the temperature is increased. Repulsive forces begin to dominate over attraction as the kinetic energy of the gas is increased and the molecules are more frequently colliding with one another. Thus $\bar{V}_{\text{Real}} > \bar{V}_{\text{Ideal}}$, and the compressibility factor is greater than unity.

C) Fill in the blanks: The two constants in the van der Waals Equation of state, a and b, are unique for every gas. The constant a is proportional to the <u>intermolecular interaction strength</u> and the constant b is proportional to the <u>intermolecular size</u>.

Answer:

In the lecture video *Gas-Liquid PV Diagrams* the van der Waals coefficients a and b were qualitatively discussed. To take a closer look at these coefficients, we can rewrite the van der Waals equation,

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

into the form

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}}$$

One can see that in the limit of a very large value of a, the second term will dominate and Z will decrease, as it should if attractive forces dominate. Likewise, in the limit of a very large b, the denominator in the first term on the right hand side of the above equation will grow small, causing this term to dominate,

and Z will increase. Think of b as a term representing the "excluded volume" of the molecules; the higher this number (thus the less actual space there is in which the molecules can move around), the higher the "real" pressure compared to the "ideal" pressure, and thus the higher the value of Z.

We can look at the origins of the a and b coefficients in even more depth by writing the formula for compressibility as a truncated power series involving B_{2V},

$$\frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{\bar{V}}. \tag{1}$$

To a first order approximation (except for very high densities), the behavior of a gas is given by the virial EOS including only the first correction as written above. The Virial equation of state will be discussed in a following lecture (you might want to come back to this after watching *The Viral Equation of State* lecture video).

We then take the van der Waals EOS, and factor $\bar{V}$ from the first denominator:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} = \frac{RT}{\bar{V}(1 - \frac{b}{\bar{V}})} - \frac{a}{\bar{V}^2} \tag{2}$$

Using the series expansion for $(1 - x)^{-1}$ when $0 \le x \le 1$ gives,

$$P = \frac{RT}{\bar{V}}\left[1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + O(\bar{V}^{-3})\right] - \frac{a}{\bar{V}^2} \tag{3}$$

Using the definition of $Z := \frac{PV}{RT}$ and the expression for P above:

$$Z = \frac{\bar{V}}{RT}\left\{\frac{RT}{\bar{V}}\left[1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + O(\bar{V}^{-3})\right] - \frac{a}{\bar{V}^2}\right\} \tag{4}$$

$$Z = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + O(\bar{V}^{-3}) - \frac{a}{RT\bar{V}} \tag{5}$$

$$Z = 1 + \frac{1}{\bar{V}}\left(b - \frac{a}{RT}\right) + \left(\frac{b}{\bar{V}}\right)^2 + O(\bar{V}^{-3}) \tag{6}$$

But we know from the lecture video slides, we also have this power series expansion for Z:

$$Z = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \cdots \tag{7}$$

and since the coefficients of same power terms must be identical, we have for the case of the terms in $\frac{1}{\bar{V}}$ that:

$$\boxed{B_{2V}(T) = b - \frac{a}{RT}} \tag{8}$$

To calculate B_{2V} we use the relationship between B_{2V} and the potential,

$$B_{2V}(T) = -2\pi N_{\mathrm{A}} \int_0^\infty \left[e^{-u(r)/k_{\mathrm{B}}T} - 1\right] r^2 \, dr.$$

To solve this, we use a hybrid potential defined as follows: For the repulsive part of the potential we will use the hard-sphere model, and for the attractive potential we will use a $\frac{1}{r^6}$ distance dependence, analogous to the Lennard-Jones model. The hybrid potential is then defined as,

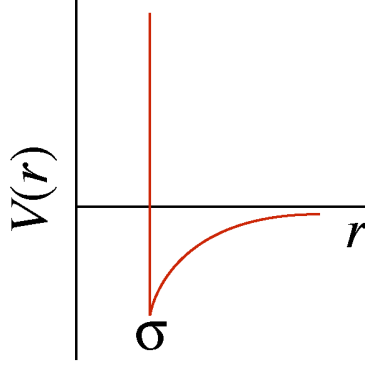$$u(r) = \begin{cases} \infty & r < \sigma \\ -\frac{c_6}{r^6} & r > \sigma \end{cases}$$

2

Figure 1: The Hybrid Potential

This potential is shown graphically here, Put in the hybrid potential and split up the integral into the two defined regions of the potential,

$$B_{2V}(T) = -2\pi N_A \left\{ \int_0^\sigma \left[e^{-\infty/k_B T} - 1 \right] r^2 \, dr + \int_\sigma^\infty \left[e^{c_6/r^6 k_B T} - 1 \right] r^2 \, dr \right\}$$

For the second term use the following series and keep the first 2 terms,

$$e^x = 1 + x + \frac{x^2}{2!} + \cdots$$

plug it in along with the fact that $e^{-\infty} = 0$,

$$B_{2V}(T) = -2\pi N_A \left\{ \int_0^\sigma -r^2 \, dr + \int_\sigma^\infty \left[1 + \frac{c_6}{r^6 k_B T} - 1 \right] r^2 \, dr \right\}$$

$$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - \frac{2\pi N_A c_6}{k_B T} \int_\sigma^\infty r^{-4} \, dr$$

$$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - \frac{2\pi N_A c_6}{k_B T} \left. \frac{1}{3} r^{-3} \right|_\sigma^\infty$$

$$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - \frac{2\pi N_A c_6}{k_B T} \left(-\frac{1}{3}\infty^{-3} + \frac{1}{3}\sigma^{-3} \right)$$

$$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - \frac{2\pi N_A c_6}{3 k_B T \sigma^3}$$

$$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - \frac{2\pi N_A^2 c_6}{3 N_A k_B T \sigma^3}$$

$$\boxed{B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - \frac{2\pi N_A^2 c_6}{3 R T \sigma^3}}$$

If we compare this to our result for the vdW EOS,

$$B_{2V}(T) = b - \frac{a}{RT}$$

3

and we find,

$$b = \frac{2\pi N_{\mathrm{A}} \sigma^3}{3} \qquad a = \frac{c_6 2\pi N_{\mathrm{A}}^2}{3\sigma^3}$$

Notice if σ is the hard sphere diameter then b is $4\times$ the volume of one mole of molecules, and $a \propto c_6$, the attractive force between the molecules. So you can see that the vdW EOS is based on a hard sphere potential at small distances and a weakly attractive potential at longer distances.

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_03`

A) The critical temperature, T_c, is best defined as:

   (a) The temperature above which a gas cannot be compressed into a liquid no matter what the pressure.

   (b) The temperature below which a gas cannot be compressed into a liquid no matter what the pressure.

   (c) The temperature below which the gas cannot be compressed into a liquid no matter what the volume.

   (d) The temperature at which the nuclei of the atoms in the gas become unstable.

   (e) The temperature at which a gas can be compressed into a liquid and coexist as a gas at the same time.

   (f) The temperature at which plasma onsets

   (g) None of the above.

Answer:
The correct answer is: the temperature above which a gas cannot be compressed into a liquid no matter what the pressure. You can see from the plot of pressure as a function of volume for CO_2 that for each isotherm (line on the pressure versus volume plot) below the critical temperature there is a flat spot on the curve. In the regions where the curve is flat, the gas and liquid can coexist. As the temperature increases, it becomes harder and harder to squeeze the gas molecules into a liquid. At some temperature, this is no longer possible, and there can no longer be a flat spot in the curve. This temperature is the critical temperature, T_c, which is represented by an inflection point on the isotherm.
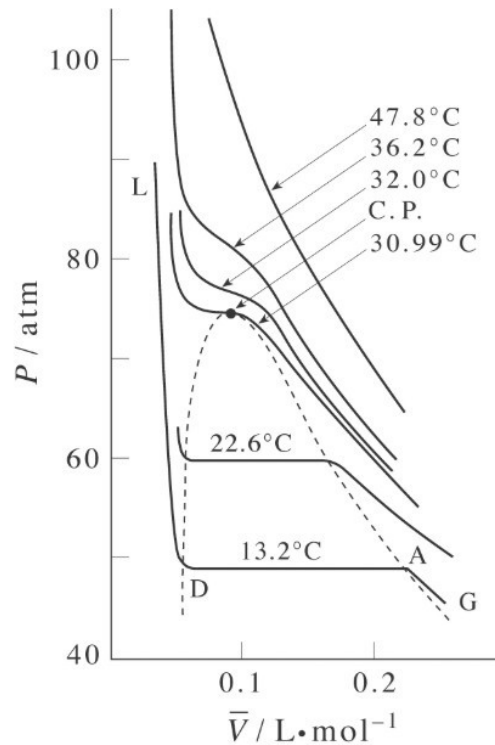
Figure 1: Pressure as a function of volume for carbon dioxide (CO_2) at several temperatures.

B) Refer to the plot below and circle the phrase in italics that best applies to the isothermal compression of carbon dioxide at 22.6 ° C.

If the container volume of the gas is decreased in the regions between the two asterisks, the pressure will (*increase* or *decrease* or *stay the same*) and in this region CO_2 exists as a (*gas* or *liquid* or *both gas and liquid*).

Answer:

We can see from the plot that in the region between the two asterisks, the pressure is constant. How can this be if the volume can take on a range of values? The answer is that, as the volume of the container which holds the gas is decreased, the gas liquefies, decreasing the amount of gas in the container. Imagine decreasing the volume from right to left in the diagram. With a small change in volume, a small amount of gas will liquefy, and the pressure will remain unchanged. At some point, however, all of the gas becomes liquid (at the left hand asterisk). Any further attempt to shrink the volume beyond this point causes a tremendous increase in the pressure, because there is only liquid left to be compressed in the region to the left of the left hand asterisk.
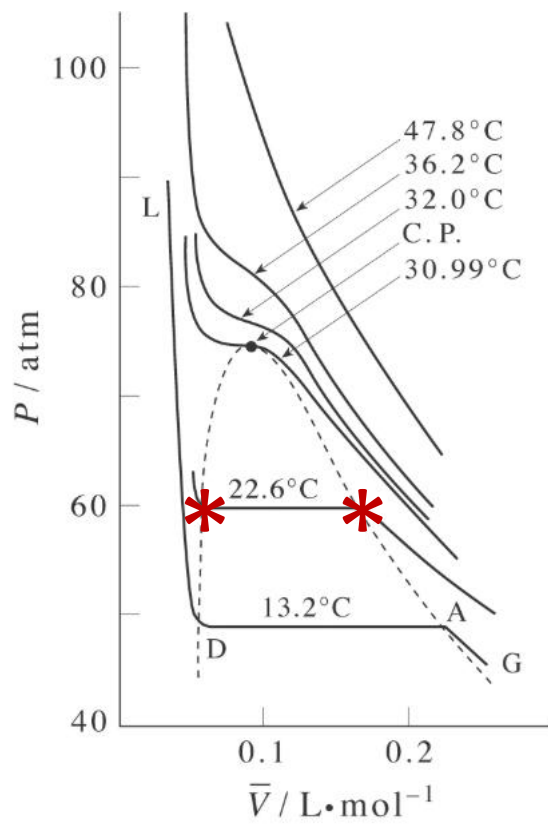
Figure 2: Pressure as a function of volume for carbon dioxide (CO_2) at several temperatures.

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_04`

A) Assign the letter(s) on the plot below that correspond to the point(s) at which all gases are at their respective critical points, _AND_ assign the letter(s) on the plot to the point at which all gases behave ideally.

   (a) A _AND_ D

   (b) $\boxed{\text{G } \underline{AND} \text{ A}}$

   (c) B _AND_ A

   (d) A _AND_ G

   (e) B,C,D,E, F _AND_ A

   (f) F _AND_ G

   (g) A _AND_ G,F

   (h) G _AND_ F

<u>Answer</u> By definition, the gas is at its critical point when the reduced temperature, T_R and reduced pressure, P_R, are equal to one, i.e., the gas is at the critical pressure and temperature, since $T_R = T/T_c$ and $P_R = P_c/P$. So, the point on the plot which correspoinds to $(P_R = 1, T_R = 1)$ is point **G**. As we know, a gas behaves ideally when $Z = 1$. This is only true at **A**. So, the answer is $\boxed{\text{G } \underline{AND} \text{ A}}$.
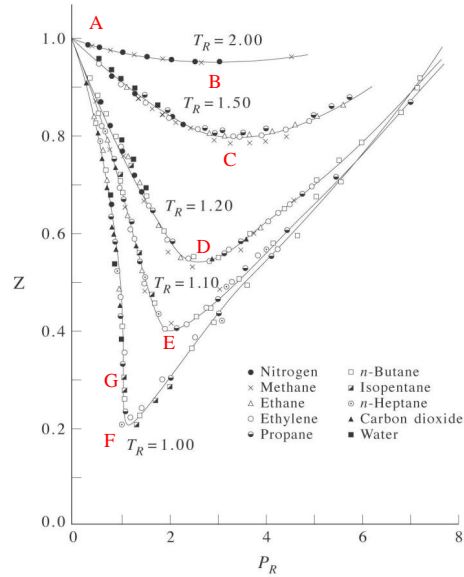
Figure 1:

B) You have a container of gas at a pressure of $P = 220$ bar and a temperature of $T = 440$ K. You are told that the critical values for this gas are $P_C = 110$ bar and $T_C = 400$ K. Using the figure below, estimate the molar volume of this gas. For this problem you may approximate the gas constant as $R \approx 0.1$ dm$^3 \cdot$ bar $\cdot$ K$^{-1} \cdot$ mol^{-1}.

(a) $\boxed{0.08 \ \ \text{dm}^3 \cdot \text{mol}^{-1}}$

(b) $0.16 \ \ \text{dm}^3 \cdot \text{mol}^{-1}$

(c) $0.04 \ \ \text{dm}^3 \cdot \text{mol}^{-1}$

(d) $0.020 \ \ \text{dm}^3 \cdot \text{mol}^{-1}$

(e) $1.0 \ \ \text{dm}^3 \cdot \text{mol}^{-1}$

Answer:

Given the information at hand it seems like a plausible plan of action is to calculate the reduced pressure, P_R and reduced temperature, T_R, and from this determine the compressibility factor Z. With Z known, we can the calculate the molar volume with the formula for compressibility. So

$$P_R = \frac{P}{P_C} = \frac{220}{110} = 2$$

$$T_R = \frac{T}{T_C} = \frac{440}{400} = 1.1$$

From the plot, at $P_R = 2$ on the isotherm T_R=1.1, $Z \approx 0.4$, therefore, if

$$Z \approx \frac{P\bar{V}}{RT},$$
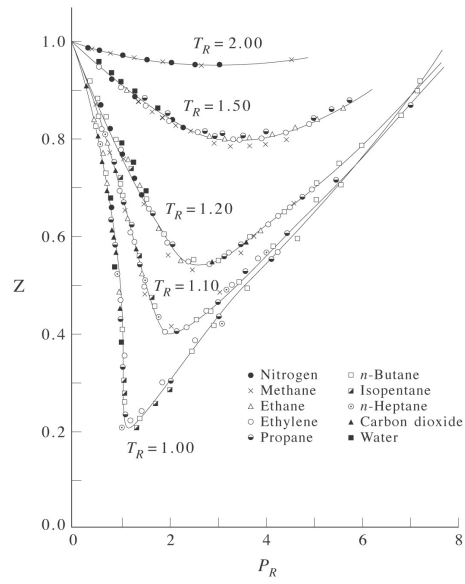
then

$$\bar{V} \approx \frac{ZRT}{P}$$

2

Figure 2:

$$\bar{V} \approx \frac{0.4 \times 0.1 \text{ dm}^3 \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 440\text{K}}{220 \text{ bar}} = 0.08 \text{ dm}^3 \cdot \text{mol}^{-1}$$

3

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_05`

A) As discussed in the lecture video,
$$B_{2V}(T) = \bar{V} - \bar{V}_{\text{Ideal}}.$$

$\boxed{TRUE}$ or *FALSE*: The sign of $B_{2V}(T)$ at low temperatures and pressures is expected to be negative.

Answer

Since attractive forces dominate at low pressures and low temperatures, it is reasonable to expect that the volume of one mole of gas would be *less* than that of an ideal gas (remember, in an ideal gas, by definition, the molecules have no interaction). So, if one were to subtract a calculated value of the molar volume for the ideal gas from its real volume, the result would be negative. Thus, according to the formula above, $B_{2V}(T)$ would be negative.

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_05`

A) As discussed in the lecture video,
$$B_{2V}(T) = \bar{V} - \bar{V}_{\text{Ideal}}.$$

$\boxed{TRUE}$ or *FALSE*: The sign of $B_{2V}(T)$ at low temperatures and pressures is expected to be negative.

Answer

Well, since attractive forces dominate at low pressures and high temperatures, it is reasonable to expect that the volume of one mole of gas would be *less* than that of an ideal gas (remember, in an ideal gas, by definition, the molecules have no interaction). So, if one were to subtract a calculated value of the molar volume for the ideal gas from its real volume, the result would be negative. Thus, according to the formula above, $B_{2V}(T)$ would be negative.

Molecular Thermodynamics
Week 2 Lecture Assessment Questions:
Ideal gases; Equations of state; PV diagrams; Molecular Interactions

May 26 - June 1, 2013

`thermovid_02_06`

A) Take a look at the plot of the Lennard-Jones potential plotted below. Determine the value of r when the potential, $u(r)$, is equal to $-\epsilon$.
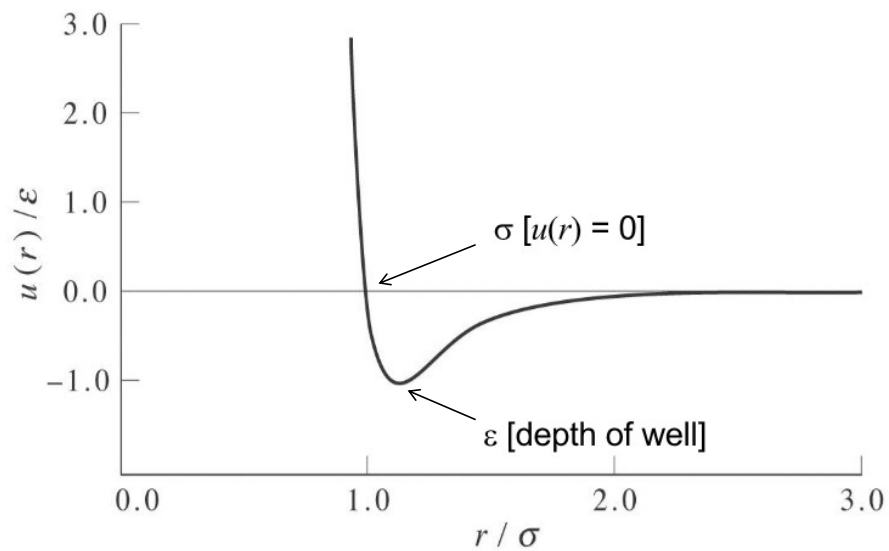

Figure 1:

(a) $-\sigma$

(b) σ

(c) 0

(d) 2σ

(e) $\boxed{2^{1/6}\sigma}$

(f) 7σ

Answer:

The easiest way to solve this problem is to recognize that $u(r) = -\epsilon$ is the point at which the potential is at its minimum. Therefore, we can take the derivative of the potential with respect to r, set this derivative equal to zero, and then solve for r to determine the value of r at the minimum:

$$\frac{\partial u}{\partial r} = 4\epsilon \left(-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right)$$

Now if we set this derivative equal to zero,

$$\frac{\partial u}{\partial r} = 4\epsilon \left(-\frac{12\sigma^{12}}{r_{min}^{13}} + \frac{6\sigma^6}{r_{min}^7} \right) = 0$$

and solve for r_{min} we get $r_{min} = 2^{1/6}\sigma$.

Molecular Thermodynamics
Week 3 Lecture Assessment Questions:

June 2 - June 8, 2013

`thermoVid_03_02`

A) For a system that has equally spaced non-degenerate energy levels, how will the partition function,

$$Q(N, V, T) = \sum_{j=1}^{\text{states}} e^{\left(\frac{-E_j(N,V)}{k_B T}\right)}$$

change if you DECREASE the temperature?

(a) $\boxed{Q \text{ will decrease}}$

(b) Q will increase

(c) Q will not change

Answer:

The partition function will decrease if you decrease the temperature. You can think about this in two ways: the first way is to recognize that if the temperature is increased, then this provides more energy to the system, and thus a greater possibility that the system will not be in its ground state. So, if the partition function is "the accessible number of energy states" then the partition function, Q, increases when the temperature increases. Likewise, when the temperature is decreased, the partition function, Q, will decrease. You can also inspect the equation for Q above and note that as T decreases, the magnitude of the exponent will increase. As the magnitude of the exponent increases, the value of the exponential function,

$$e^{\left(\frac{-E_j(N,V)}{k_B T}\right)}$$

decreases, and thus Q decreases with decreasing temperature.

Molecular Thermodynamics
Week 3 Lecture Assessment Questions:

June 2 - June 8, 2013

`thermoVid_03_04`

A) What could be the units for molar heat capacity?

   (a) $\frac{KJ}{mol}$

   (b) $\frac{J}{mol\ K}$

   (c) $\frac{kcal}{mol\ K}$

   (d) $\frac{mol\ K}{kJ}$

   (e) $\frac{J}{mol}$

   (f) first and third options above

   (g) $\boxed{\text{second and third options above}}$

   (h) none of the above

<u>Answer:</u>

Recall that the molar heat capacity is defined as the energy required to raise the temperature of one mole of a substance by $1\ K$. This is the equivalent of saying it is an amount of energy, per mole, per K, or energy/mole/$K \rightarrow$ energy/(mole K). You can also think about it like this: if you have a known heat capacity, and you multiply it by the temperature change for one mole of that substance, you should get back the amount of energy that has been added to that one mole of substance. The temperature, T, should cancel, i.e.;

$$\frac{\text{Energy}}{\text{mol K}} \cdot K \rightarrow \frac{\text{Energy}}{\text{mol}}$$

So of all the possible answers, b) has the correct units, and so does c) (recall you can easily convert between calories and joules with the conversion factor 4.184 joules/calorie).

Molecular Thermodynamics
Week 3 Lecture Assessment Questions:

June 2 - June 8, 2013

`thermoVid_03_05`

A) Comparing the trial partition function,

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V-Nr)^N e^{\frac{\beta s N^2}{V}}$$

to the ideal gas partition function,

$$Q(N,V,\beta) = \frac{[q(V,T,\beta)]^N}{N!} \quad \text{where } q = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2}V$$

what will be true as the gas to which the trial partition function belongs becomes more dilute?

(a) the partition function will become closer to that of an ideal gas.

(b) the partition function will become less like that of an ideal gas.

(c) the partition function will not change, since it is not a function of the volume.

(d) the partition function will become more similar to that of a real van der Waals gas.

(e) the dilution of the gas will have no effect on the partition function.

<u>Answer:</u>

Correct answer is: the trial partition function becomes closer to the ideal gas partition function as the gas becomes more dilute. Imagine a container of constant volume, and in it you place progressively fewer and fewer molecules. This means that N is decreasing, and the gas is becoming more dilute. In the extreme case, as $N \to 0$, the term Nr vanishes, and the exponential term $e^{\frac{\beta s N^2}{V}} \to 1$.

B) Given the expression for $\ln Q$ provided in the lecture,

$$\ln Q = \frac{3}{2}N(\ln 2\pi m - \ln h^2 - \ln\beta) + N\ln(V-Nr) + \frac{s\beta N^2}{V} - \ln N!$$

what is the internal energy for a van der Waals gas?

(a) $\frac{3}{2}\frac{N}{k_B T} - \frac{sN^2}{V}$

(b) $\frac{3}{2}\frac{N}{k_B T}$

(c) $\frac{3}{2}Nk_B T$

(d) $\frac{3}{2}Nk_B T - \frac{sN^2}{V}$

(e) $\frac{3}{2}Nk_BT + \frac{sk_B^2T^2N^2}{2V}$

(f) $\frac{2}{3N}kT - \frac{sk_B^2T^2N^2}{2V}$

(g) $\frac{2}{3N}kT - \frac{sN^2}{V}$

Answer:

From lecture 3.1 we know,

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,T}$$

We are given the natural log of the partition function, so we must take the derivative of this function to find $\langle E \rangle$. Recall that all terms that do not contain β are constant and thus the derivatives of these terms are zero. This greatly simplifies the math, and thus we are left with taking the derivative of two terms,

$$-\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,T} = -\frac{\partial}{\partial \beta}\left(\frac{3}{2}N(\ln 2\pi m - \ln h^2 - \ln\beta) + N\ln(V - Nr) + \frac{s\beta N^2}{V} - \ln N!\right) \tag{1}$$

$$= -\frac{\partial}{\partial \beta}\left(\frac{3}{2}N(-\ln\beta) + \frac{s\beta N^2}{V}\right) \tag{2}$$

$$= \frac{3}{2}\frac{N}{\beta} - \frac{sN^2}{V} \tag{3}$$

$$= \frac{3}{2}\frac{N}{(1/k_BT)} - \frac{sN^2}{V} \tag{4}$$

$$= \frac{3}{2}Nk_BT - \frac{sN^2}{V} \tag{5}$$

Molecular Thermodynamics
Week 3 Lecture Assessment Questions:

December 27, 2013

`thermoVid_03_06`

A) If the energy of a molecular system can be written as the sum of three independent contributions, $E = \epsilon_A + \epsilon_B + \epsilon_C$, then what is the correct expression for the molecular partition function, q, in terms of the individual contributions?

    (a) $q = q_A + q_B + q_C$

    (b) $q = \sum_j \ln q_j$

    (c) $q = 3q_A$

    (d) $\boxed{q = q_A q_B q_C}$

    (e) $q = e^{q_A} e^{q_B} e^{q_C}$

    (f) $q = \ln q_A + \ln q_B + \ln q_C$

    (g) none of the above

Answer:

If the energy can be written as the sum of three independent terms, this means

$$
\begin{aligned}
E =& \epsilon_A + \epsilon_B + \epsilon_C \\
=& - \left(\frac{\partial \ln q}{\partial \beta} \right) \\
=& - \frac{\partial \ln}{\partial \beta} \left(\sum_{i,j,k} e^{-\beta[\epsilon_i^A + \epsilon_j^B + \epsilon_k^C]} \right) \\
=& - \frac{\partial \ln}{\partial \beta} \left(\sum_i e^{-\beta \epsilon_i^A} \sum_j e^{-\beta \epsilon_j^B} \sum_k e^{-\beta \epsilon_k^C} \right) \\
=& - \frac{\partial \ln}{\partial \beta} \left(q_A q_B q_C \right)
\end{aligned}
$$

and thus $q = q_A q_B q_C$.

Molecular Thermodynamics
Week 3 Lecture Assessment Questions:

December 27, 2013

`thermoVid_03_07`

A) If the total energy of a molecule, ε, is given by $\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{elec}}$, then the total molecular partition function, $q(V,T)$, is given by,

(a) $q(V,T) = q_{\text{trans}} + q_{\text{vib}} + q_{\text{rot}} + q_{\text{elec}}$

(b) $\boxed{q(V,T) = q_{\text{trans}}q_{\text{vib}}q_{\text{rot}}q_{\text{elec}}}$

(c) $\dfrac{1}{q_{\text{trans}}+q_{\text{vib}}+q_{\text{rot}}+q_{\text{elec}}}$

(d) $\dfrac{1}{q_{\text{trans}}q_{\text{vib}}q_{\text{rot}}q_{\text{elec}}}$

(e) none of the above

Answer:

In this problem we are discussing real, physical properties of a molecular system - electronic, translational, vibrational and rotational energy states - not just hypothetical properties A,B and C as discussed in lecture 3.6; however, the solution is similar. If the energy can be written as the sum of four independent terms, this means

$$
\begin{aligned}
E =& \varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{elec}} \\
=& -\left(\frac{\partial \ln q(V,T)}{\partial \beta}\right)_V \\
=& -\frac{\partial \ln}{\partial \beta}\left(\sum_{i,j,k,l} e^{-\beta[\varepsilon_i^{\text{trans}}+\varepsilon_j^{\text{vib}}+\varepsilon_k^{\text{rot}}+\varepsilon_l^{\text{elec}}]}\right) \\
=& -\frac{\partial \ln}{\partial \beta}\left(\sum_{i} e^{-\beta\varepsilon_i^{\text{trans}}}\sum_{j} e^{-\beta\varepsilon_j^{\text{vib}}}\sum_{k} e^{-\beta\varepsilon_k^{\text{rot}}}\sum_{l} e^{-\beta\varepsilon_l^{\text{elec}}}\right) \\
=& -\frac{\partial \ln}{\partial \beta}\left(q_{\text{trans}}q_{\text{vib}}q_{\text{rot}}q_{\text{elec}}\right)
\end{aligned}
$$

and thus $q(V,T) = q_{\text{trans}}q_{\text{vib}}q_{\text{rot}}q_{\text{elec}}$.

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

December 27, 2013

`thermo_vid_4_1`

A) We made the approximation

$$\int_1^\infty dn e^{-\frac{\beta h^2 n^2}{8ma^2}} \approx \int_0^\infty dn e^{-\frac{\beta h^2 n^2}{8ma^2}}.$$

The difference is

$$\int_0^1 dn e^{-\frac{\beta h^2 n^2}{8ma^2}}.$$

This integral cannot be solved analytically, but what is it roughly equal to for methane?

(a) 0

(b) $\sqrt{\pi}$

(c) ∞

(d) $\boxed{1}$

(e) 42

(f) 2

<u>Answer:</u>
The answer is 1. The exponential that is the argument of the integral can be evaluated at both definite limits in the integral

$$\int_0^1 dn e^{-\beta h^2 n^2/8ma^2}$$

Considering first the limit of 1, we need to know $e^{-\beta h^2 n^2/8ma^2}$ for $n = 1$. If we choose SI units, note that the magnitude of h^2 will be on the order of 10^{-67}, while the mass of methane will be on the order of 10^{-24}, and even a box having a side length of atomic scale would result in a^2 being on the order of 10^{-20}. Thus, the argument of the exponential will be effectively zero, and hence the argument of the integral will be effectively 1. At the integral limit of 0, the argument of the integral is $e^{-0} = 1$ rigorously. This makes the integral itself effectively an integral only of dn over a definite interval of width 1, which is, of course, equal to 1. We may note that 1 is indeed negligibly small compared to 10^{30} (q_{trans} from the prior slide of this video), so the approximation employed to permit the solution of the integral is a very good one!

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

January 26, 2014

`thermo_vid_4_2`

A) The fluorine atom has a ground-state degeneracy of 4, and a first excited state at 404 cm^{-1} with a degeneracy of 2. What is q_{elec} for F at 500 K?

    (a) 4

    (b) 6.43

    (c) 0

    (d) $\boxed{4.63}$

    (e) ∞

Answer:
Because this is a halogen atom, we'll want to keep both of the first two terms, as outlined in the lecture slides, and then apply the formula

$$q_{elec} = g_o e^{-\beta \epsilon_o} + g_1 e^{-\beta \epsilon_1}.$$

To evaluate the second term, it will be easiest to work with Boltzmann's constant expressed in wavenumbers. Recalling from the first week of the course,

$$E = h\nu = \frac{hc}{\lambda}$$

If we divide both sides by hc we obtain

$$\frac{E}{hc} = \frac{1}{\lambda}$$

Recall that 1 J is equal to 1 kg m^2/s^2, thus if we consider an energy of 1 J

$$\frac{1 \text{ J}}{hc} = \frac{1 \text{kg m}^2/\text{s}^2}{6.626 \times 10^{-34}(\text{kg m/s})2.998 \times 10^{10}(\text{cm/s})} = \frac{1}{\lambda}$$

and thus there are 1.98647×10^{-23} joules per wavenumber. Now we convert Boltzmann's constant,

$$1.38064 \times 10^{-23} \text{ J/K} \cdot \left[1 \text{ cm}^{-1}/(1.98647 \times 10^{-23} \text{ J}) \right] = 0.6950 \text{ cm}^{-1}/\text{K}$$

Now we can calculate the electronic partition function for Fluorine.

$$q_{\text{elec}} = 4e^0 + 2e^{\frac{-404\text{cm}^{-1}}{0.6950 \text{ cm}^{-1}/\text{K} \cdot 500\text{K}}} = 4 + 0.6254 = 4.6254$$

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

June 9 - June 16, 2013

`thermo_vid_4_3`

A) What is the partial derivative of $g_2 e^{-\beta \epsilon_2}$ with respect to T?

(a) $\boxed{g_2 \epsilon_2 \frac{e^{-\beta \epsilon_2}}{k_B T^2}}$

(b) $g_2 \epsilon_2 e^{-\beta \epsilon_2}$

(c) $-g_2 \epsilon_2 \frac{e^{-\beta \epsilon_2}}{k_B T^2}$

(d) $g_2 \frac{e^{-\beta \epsilon_2}}{k_B T^2}$

Answer:

Lets call $f = g_2 e^{-\beta \epsilon_2}$. To solve this we can use the chain rule, recalling that $\beta = 1/k_B T$,

$$
\begin{aligned}
\frac{\partial f}{\partial T} &= \frac{\partial f}{\partial \beta} \frac{\partial \beta}{\partial T} \\
&= g_2 \frac{\partial}{\partial \beta} e^{-\beta \epsilon_2} \frac{\partial \beta}{\partial T} \\
&= -g_2 \epsilon_2 e^{-\beta \epsilon_2} \frac{\partial \beta}{\partial T} \\
&= -g_2 \epsilon_2 e^{-\beta \epsilon_2} \frac{-1}{k_B T^2} \\
&= g_2 \frac{\epsilon_2 e^{-\beta \epsilon_2}}{k_B T^2}
\end{aligned}
$$

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

June 9 - June 16, 2013

`thermo_vid_4_4`

A) Given that we can model the vibrational energy levels of a diatomic molecule according to the harmonic oscillator expression, $\varepsilon_n = \left(n + \frac{1}{2}\right) h\nu$, the correct expression for the vibrational partition function is,

(a) $q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)h\nu}$

(b) $q_{\text{vib}} = e^{-\beta\left(n+\frac{1}{2}\right)h\nu}$

(c) $q_{\text{vib}} = \sum_{n=0}^{\infty} \ln\left\{-\beta\left(n+\frac{1}{2}\right)h\nu\right\}$

(d) $q_{\text{vib}} = \ln\left\{-\beta\left(n+\frac{1}{2}\right)h\nu\right\}$

(e) none of the above

Answer:

The partition function written in its most general form is,

$$q = \sum_{i=1}^{\infty} e^{-\beta\epsilon_i}.$$

Given that the energy levels of a harmonic oscillator are

$$\epsilon_n = \left(n + \frac{1}{2}\right) h\nu, \quad v = 0, 1, 2, 3, \dots$$

we can directly substitute to obtain,

$$q = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)h\nu}$$

B) Which of the following is a correct expression for the *fraction* of diatomic molecules that are *not* in the lowest vibrational energy state?

(a) $f_{n>0} = 1 - e^{-\beta E_{n=0}}$

(b) $f_{n>0} = e^{-\beta E_{n=0}} - 1$

(c) $f_{n>0} = 1 - \frac{e^{-\beta E_{n=0}}}{\sum_{n=0}^{\infty} e^{-\beta E_n}}$

(d) $f_{n>0} = 1 - \frac{\sum_{n=0}^{\infty} e^{-\beta E_n}}{e^{-\beta E_{n=0}}}$

(e) $f_{n>0} = \frac{e^{-\beta E_{n=0}}}{\sum_{n=1}^{\infty} e^{-\beta E_n}} - 1$

(f) $f_{n>0} = \frac{\sum_{n=0}^{\infty} e^{-\beta E_n}}{e^{-\beta E_{n=0}}} - 1$

<u>Answer:</u> If you refer back to lecture video 3.2, you'll see that the equation,

$$p_j = \frac{e^{-\beta E_j}}{\sum_{j=1}^{\infty} e^{-\beta E_j}}$$

was provided as the means to compute the probability p_j of being in state j. We want to determine the probability that the system is *not* in the ground state. Since the probability that it is in *some* state is 1, we can subtract the probability that it *is* in the ground state to determine the desired answer. The probability that it is in the ground vibrational state is,

$$\frac{e^{-\beta E_{n=0}}}{\sum_{n=0}^{\infty} e^{-\beta E_n}},$$

therefore, the probability that the diatomic molecule is *not* in its lowest vibrational energy state is

$$1 - \frac{e^{-\beta E_{n=0}}}{\sum_{n=0}^{\infty} e^{-\beta E_n}}$$

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

June 9 - June 16, 2013

`thermo_vid_4_5`

A) If you assume that only translational and rotational degrees of freedom contribute, at 300 K which of the following gasses will have the *smallest* constant volume molar heat capacity, $\bar{C}_V$?

   (a) molecular fluorine (F_2)

   (b) molecular iodine (I_2)

   (c) molecular chlorine (Cl_2)

   (d) molecular hydrogen (H_2)

   (e) If only translations and rotations contribute, all of these gases will have the same value for $\bar{C}_V$.

Answer:

The contribution from the translational degrees of freedom to the heat capacity is $(3/2)R$ per mole, and the contribution from the rotational degrees of freedom is $(1/2)R$ per each degree of freedom per mole. A diatomic molecule has 2 degrees of rotational freedom, thus the total molar heat capacity is $(5/2)R$ for a diatomic molecule if the vibrational component is ignored. Since all of the molecules listed are diatomics, the correct answer is: e) If only translations and rotations contribute, all of these gases will have the same value for $\bar{C}_V$.

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

December 27, 2013

`thermo_vid_4_6`

A) For a diatomic ideal gas, which of the following makes the *largest* contribution to the total molar heat capacity, $\bar{C}_V$, at temperatures below 1000 K?

   (a) $\boxed{\text{translation}}$

   (b) rotation

   (c) vibration

   (d) electronic

   (e) they all contribute the same amount to $\bar{C}_V$

Answer:

If you look at the last slide in lecture video 4.4 that plots $\bar{C}_{V,vib}$ as a function of T, you will see that the maximum contribution to $\bar{C}_{V,vib}$ is R. This is also true for $\bar{C}_{V,rot}$, where each of the two rotational degrees of freedom contribute $(1/2)R$ for a total of R. At ordinary temperatures, the electronic degrees of freedom contribute very little to the heat capacity. The translational degrees of freedom contribute $(3/2)R$, so this is the correct answer (at *all* temperatures).

B) Given

$$\bar{C}_{V,vib} = R \left(\frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{(1 - e^{-\Theta_{vib}/T})^2}$$

and a vibrational temperature for $^{79}\text{Br}_2$ of 465 K, what is the vibrational heat capacity of bromine gas at 500 K expressed as a multiple of R?

   (a) $0.06R$

   (b) $0.42R$

   (c) $0.61R$

   (d) $\boxed{0.93R}$

To find the answer we need simply to plug in the numbers,

$$R \left(\frac{465\text{K}}{500\text{K}} \right)^2 \frac{e^{-465\text{K}/500\text{K}}}{(1 - e^{-(465\text{K}/500\text{K})})^2} = 0.93R$$

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

December 27, 2013

`thermo_vid_4_7`

A) What is the ratio of the rotational heat capacity for a nonlinear polyatomic ideal gas compared to that for a linear polyatomic ideal gas at high temperature?

    (a) 1

    (b) ⟦1.5⟧

    (c) 2.0

    (d) 3

    (e) it depends on the number of atoms

    (f) None of the above

<u>Answer:</u>

A linear polyatomic molecule has 2 degrees of rotational freedom, the same number as a diatomic molecule. A non-linear polyatomic molecule, however, has 3 rotational degrees of freedom. Thus, if each rotational degree of freedom contributes $(1/2)R$ to the heat capacity (high-temperature limit), then for the linear molecule, $\bar{C}_{V,rot} = R$ and for the non-linear molecule $\bar{C}_{V,rot} = (3/2)R$. The correct answer is therefore 1.5.

Molecular Thermodynamics
Week 4 Lecture Assessment Questions:

December 27, 2013

`thermo_vid_4_8`

A) You have a molecule containing 4 atoms. As you heat its gas to very, very high temperature, you observe the heat capacity approaching an asymptotic value of $9.5R$. Is your molecule linear or non-linear?

(a) $\boxed{\text{linear}}$

(b) non-linear

<u>Answer:</u>

If the molecule has $n = 4$ atoms, then if it is linear it has $3 \cdot 4 - 5 = 7$ vibrational degrees of freedom. Likewise, for a non-linear molecule, there are $3 \cdot 4 - 6 = 6$ vibrational degrees of freedom. At high temperatures, each vibrational degree of freedom contributes R to the heat capacity. As previously established, at high temperature for a linear molecule $\bar{C}_{V,rot} = R$, while for a non-linear molecule $\bar{C}_{V,rot} = (3/2)R$. The translational degrees of freedom contribute $(3/2)R$ independent of molecular geometry. Thus, for the non-linear molecule, adding up the various contributions we have: $6R$ (vibrational) + $(3/2)R$ (rotational) + $(3/2)R$ (translational) = $9R$. For the linear molecule, we have: $7R$ (vibrational) + $1R$ (rotational) + $(3/2)R$ (translational) = $9.5R$. So the correct answer is that the molecule is linear.

Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

December 29, 2013

`thermo_vid_5_1`

A) If the internal pressure of 1 L of an ideal gas is twice the external pressure, by how much will the volume of the gas expand as it does work on the surroundings if the temperature is held constant?

  (a) the gas will not expand

  (b) 0.5 L

  (c) $\boxed{1 \text{ L}}$

  (d) 2 L

<u>Answer:</u>

We know from the ideal gas law that $P_1 V_1 = P_2 V_2$ if the temperature is held constant, and thus,

$$V_2 = \frac{P_1 V_1}{P_2}.$$

So, putting this in the context of the problem, $P_1 = 2P_{\text{ext}}$, $P_2 = P_{\text{ext}}$, and $V_1 = 1$ L,

$$V_2 = \frac{2P_{\text{ext}} 1 \text{ } L}{P_{ext}} = 2 \text{ L}$$

The gas doubles its volume, and therefore increases its volume by 1 L, from 1 L to 2 L.

Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

December 29, 2013

`thermo_vid_5_2`

A) Calculate the work done by the reversible isothermal expansion of an ideal gas from a pressure of $P_1 = 1$ bar and a volume of $V_1 = 2$ dm^3 to a final pressure of $P_2 = 0.25$ bar. Hint: It might be helpful to remember that 1 bar $\cdot$ dm$^3 = 100$ J.

  (a) $w_{rev} = -800$ J

  (b) $w_{rev} = -400$ J

  (c) $\boxed{w_{rev} = -280 \text{ J}}$

  (d) $w_{rev} = -140$ J

  (e) $w_{rev} = -100$ J

  (f) $w_{rev} = 100$ J

  (g) $w_{rev} = 140$ J

  (h) $w_{rev} = 280$ J

  (i) $w_{rev} = 400$ J

  (j) $w_{rev} = 800$ J

<u>Answer:</u>

$$\text{At constant } T: \ nRT = P_1V_1 = P_2V_2 \quad \text{so} \quad V_2 = \frac{P_1V_1}{P_2} = \frac{1 \text{ bar} \cdot 2 \text{ dm}^3}{0.25 \text{ bar}} = 8 \text{ dm}^3$$

As this is a reversible expansion, we may use $P_{\text{ext}} = nRT/V$, and

$$w = -\int_{V_1}^{V_2} P_{\text{ext}} dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1} = -P_1V_1 \ln \frac{V_2}{V_1}$$

$$w = -(1 \text{ bar}) \left(2 \text{ dm}^3\right) \ln \frac{8 \text{ dm}^3}{2 \text{ dm}^3} = (-2 \text{ bar} \cdot \text{dm}^3) \ln(4) = (-2 \text{ bar} \cdot \text{dm}^3)(1.4)$$

$$w = -2.8 \text{ bar} \cdot \text{dm}^3 \cdot \frac{100 \text{ J}}{1 \text{ bar} \cdot \text{dm}^3} = -280 \text{ J}$$

Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

December 29, 2013

`thermo_vid_5_3`

A) The molar energy of an ideal diatomic gas depends on,

    (a) pressure

    (b) volume

    (c) $\boxed{\text{temperature}}$

    (d) all of the above

    (e) none of the above

<u>Answer:</u>

To summarize, if you look back to the lecture videos from week 4, you will see that,

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$$= \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{rot}} \cdot \frac{e^{-\theta_{\text{vib}}/2T}}{1 - e^{-\theta_{\text{vib}}/T}} \cdot g_{el} e^{D_e/k_B T}$$

for an ideal diatomic gas. And we know that,

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

and

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

When we take the natural log of this function we have,

$$\ln q = \frac{3}{2}\ln T + \ln T - \frac{\Theta_{\text{vib}}}{2T} - \ln(1 - e^{-\Theta_{\text{vib}}/T}) + \frac{D_e}{k_B T} + \text{terms not containing T}$$

The terms in this function involve only T, not P or V. Thus, the molar energy (for which $N = N_A$) depends only upon the temperature.
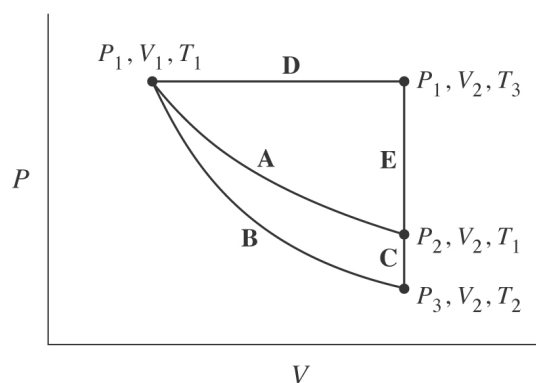
Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

December 29, 2013

`thermo_vid_5_5`

A) Compare the reversible isothermal expansion of an ideal gas to the reversible adiabatic expansion of that same ideal gas, corresponding to Path A and Path B on the plot below.

Which of the following is a TRUE statement.

(a) Both paths do the same amount of work on the surroundings.

(b) The adiabatic path does more work on the surroundings than the isothermal path.

(c) The isothermal path does more work on the surroundings than the adiabatic path.

In the adiabatic case, the gas cools as energy is converted to work with no opportunity for heat to flow in to compensate. As a result, path B finishes at a lower pressure, and it does less work on the surroundings. The isothermal path allows energy as heat to flow back into the gas as it expands to maintain the temperature, and as a result the gas finishes at a higher pressure and ends having done more work on the surroundings.

Graphically, one can see that the area under the curve, which is the work, i.e

$$w = -\int_{V_1}^{V_2} P dV$$

is clearly smaller for the case of curve B than for curve A. Again, the work done on the surroundings is greater for the isothermal expansion than for the adiabatic expansion.

B) Which will cool more when expanding adiabatically into a volume ten times larger than originally occupied, a monatomic ideal gas or a diatomic ideal gas?

1

(a) $\boxed{\text{monatomic}}$

(b) diatomic

Answer:

The monatomic gas will cool more. There is nowhere to draw energy from in the case of a monatomic gas except from the translational modes, and the temperature is determined from only these translational modes (which describe the kinetic energy of the molecules). Mathematically, we can recall the monatomic case that was developed in the lecture video,

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \left(\frac{V_1}{V_2}\right)$$

Imagine if instead we derive this equation for a diatomic molecule. Then we would have, in the high temperature limit,

$$\left(\frac{T_2}{T_1}\right)^{7/2} = \left(\frac{V_1}{V_2}\right)$$

because each of the two rotational degrees of freedom contributes $R/2$ to the heat capacity, and the one vibrational mode contributes R. Even below the high temperature limit, the exponent would nevertheless be *greater* than $3/2$ (the minimum is $5/2$, if the temperature is well below the vibrational temperature). Given that the exponent in the above equation for the diatomic gas must be greater than the $3/2$ appropriate for the monatomic gas, the ratio of T_2/T_1 would necessarily have to be *larger* relative to the monatomic gas (since $V_1/V_2 < 1$), and thus the gas would cool less (since $T_2 < T_1$).

Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

June 16 - June 22, 2013

`thermo_vid_5_7`

A) For a process (such as a chemical reaction) at constant pressure, the heat, q_P, is a state function if the only work that can be done is pressure-volume work.

   (a) $\boxed{\text{TRUE}}$ (For constant pressure, $q_P = \Delta H$)

   (b) FALSE

<u>Answer:</u>

As described in lecture video 5.7,

$$q_p = \Delta U + P_{\text{ext}} \int_{V_1}^{V_2} dV = \Delta U + P\Delta V$$

and from this a new state function is defined as $H = U + PV$.

At constant pressure, $\Delta H = \Delta U + P\Delta V$, and therefore $q_p = \Delta H$, and thus it is a state function. Both the differentials of U and V (at constant pressure) are integrated in their normal way.

Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

June 16 - June 22, 2013

`thermo_vid_5_8`

A) Which of the following is true:

    (a) $\boxed{C_p \text{ is generally larger than } C_v.}$

    (b) C_v is generally larger than C_p

    (c) C_p is generally equal to C_v.

<u>Answer:</u>

As you will see in the remainder of this video, C_p is generally larger than C_v because extra heat is required to do PV work at constant pressure that is *not* done at constant volume.
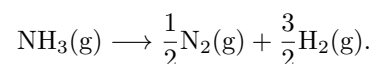
Molecular Thermodynamics
Week 5 Lecture Assessment Questions:

June 16 - June 22, 2013

`thermo_vid_5_9`

A) Consider the following endothermic reaction at 298 K and 1 bar,

$$\text{NH}_3(\text{g}) \longrightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}).$$

Which of the following statements is true?

(a) $\Delta_\text{r}\bar{H} = 0$

(b) $\Delta_\text{r}\bar{H} < 0$

(c) $\Delta_\text{r}\bar{H} < \Delta_\text{r}\bar{U}$

(d) $\boxed{\Delta_\text{r}\bar{U} < \Delta_\text{r}\bar{H}}$

<u>Answer:</u>

Well, we can rule out $\Delta_r H = 0$ right away - the question states that the reaction is endothermic, so there is some quantity of heat transferred. Since it is endothermic, heat is transferred *from* the surroundings *to* the system, and therefore the sign of $\Delta_r H$ is positive, so $\Delta_r H < 0$ cannot be the correct answer. Also $\Delta_r H = \Delta_r U + P\Delta V$, and clearly ΔV is positive as we can see from the reaction: one mole of gas reacts to form two moles of gaseous products. So the proper answer is $\Delta_\text{r}\bar{U} < \Delta_\text{r}\bar{H}$.
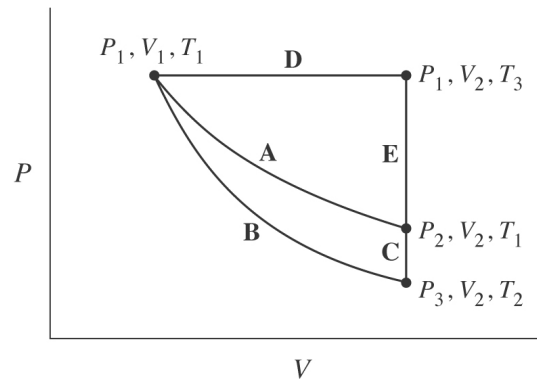
`Thermo_Vid_06_02`

A) The diagram below is the "ideal gas roadmap" that is shown in this lecture video. What is the entropy change for path **E**?

(a) $\boxed{\int_{T_3}^{T_1} \frac{C_V}{T} dT}$

(b) $\int_{T_3}^{T_2} \frac{C_V}{T} dT$

(c) $\int_{T_3}^{T_2} \frac{C_V}{V} dV$

(d) $\int_{T_3}^{T_1} C_V dT$

(e) $\int_{T_3}^{T_1} C_P dT$

(f) $\int_{T_3}^{T_1} \frac{C_P}{P} dT$

Answer:

We know that the volume is constant along path **E** and therefore there is no work done, thus

$$\Delta U = q_{\mathrm{rev,E}} = \int_{T_3}^{T_1} C_V dT$$

From the second law,

$$\Delta S = \frac{q_{rev}}{T}$$
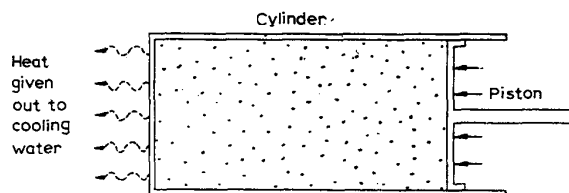$$= \int_{T_3}^{T_1} \frac{C_V}{T} dT$$

1

Molecular Thermodynamics
Week 6 Lecture Assessment Questions:

June 23 - June 30, 2013

`Thermo_Vid_06_03`

A) The figure below depicts the isothermal compression of an ideal gas.

If the compression is carried out reversibly, and we define the gas as the system and everything else as the surroundings, which of the following statements is TRUE for this process?

(a) The entropy of the system will increase.

(b) The entropy of the surroundings will increase.

(c) The total entropy, system + surroundings, will increase.

(d) The entropy of the surroundings will not change.

(e) The entropy of the system will not change.

<u>Answer:</u>

This is a *reversible* process, so the TOTAL entropy change,

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

and thus $\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$. The process isothermal, and we know that the energy of an ideal gas depends only upon its temperature, so, $\Delta U = \delta q + \delta w = 0$, and therefore $\delta q = -\delta w$. Work is done *on* the system, and by sign convention, this work is positive, so δq_{system} must be negative, which means that $\delta q_{\text{surroundings}}$ is positive. Given that $dS_{\text{surroundings}} = \frac{\delta q}{T}$, the answer must be that the entropy of the surroundings will increase. The entropy of the system (the gas) will not increase, since δq is negative, and the total entropy will not increase because the compression is reversible. The entropy of the surroundings does in fact change in an amount equal and opposite to that of the system. Therefore, the only correct answer is that the entropy of the surroundings will increase.

Molecular Thermodynamics
Week 6 Lecture Assessment Questions:

June 23 - June 30, 2013

`Thermo_Vid_06_04`

A) What is the maximum value of W for 6 things being distributed into 4 degenerate subgroups?

    (a) 720

    (b) 24

    (c) 6.20×10^{23}

    (d) 120

    (e) 2.58×10^{22}

    (f) $\boxed{180}$

Answer:

We have 6 distinguishable objects that can be arranged into 4 groups. Here, the number of possible groups is less than the number of objects. The maximum value of W will occur when each group contains the minimum number of objects. In this case, since there are four groups, two of the groups must have two objects each and the other two groups only one object; thus,
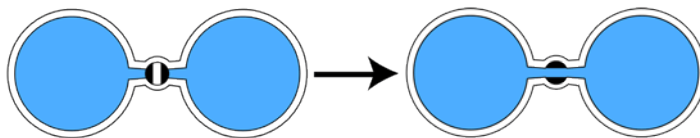
$$W = \frac{6!}{2! \times 2! \times 1! \times 1!} = 180$$

1

Molecular Thermodynamics
Week 6 Lecture Assessment Questions:

June 23 - June 30, 2013

`Thermo_Vid_06_05`

A) Imagine you have two containers of equal volume separated by a valve. In each container there is one mole of the same ideal, monatomic gas.

What is the change in entropy for this system if the valve is initially closed and you open it, $\Delta S_{\text{closed}\rightarrow\text{open}}$? Assume the volume of the valve is negligible.

(a) $\Delta S_{\text{closed}\rightarrow\text{open}} = -2R\ln 2$

(b) $\Delta S_{\text{closed}\rightarrow\text{open}} = -R\ln 2$

(c) $\Delta S_{\text{closed}\rightarrow\text{open}} = -2R$

(d) $\boxed{\Delta S_{\text{closed}\rightarrow\text{open}} = 0}$

(e) $\Delta S_{\text{closed}\rightarrow\text{open}} = 2R$

(f) $\Delta S_{\text{closed}\rightarrow\text{open}} = R\ln 2$

(g) $\Delta S_{\text{closed}\rightarrow\text{open}} = 2R\ln 2$

<u>Answer:</u>

This is a surprisingly difficult problem and is known as the Gibbs Paradox (Wikipedia has a nice page dedicated to it). Perhaps the easiest way to look at it is (i) we have neither compressed nor expanded either gas, so no work is done, (ii) therefore, the internal energy change is equal to the heat transfer, but the two gases are at the same temperature, so there is no heat transfer, (iii) since $\delta q_{rev} = 0$ then $\delta S = 0$.

A different way to see it is to consider, what if you were to close the valve again? The entropy of a system cannot spontaneously decrease. So, if the entropy had *increased* upon opening the valve, returning the system to its original state by closing the valve would *decrease* the entropy, which is not allowed. Hence, the entropy change for either opening or closing the valve must be zero.

Note that the indistinguishability of the gas particles is crucial to all of this analysis.

Molecular Thermodynamics
Week 6 Lecture Assessment Questions:

June 23 - June 30, 2013

`Thermo_Vid_06_06`

A) For an ideal monatomic gas, the contribution to the entropy from translation increases with the mass of the atom because the spacings between the translational energy levels get larger.

(a) TRUE

(b) ⟨ FALSE ⟩

Answer:

It is true that the contribution to the entropy from translation *does* increase with the mass of the atom, but not because the energy spacings between the average energy levels get larger with increasing atomic mass - the energy spacings actually get smaller! This, in turn, increases the number of available states (and thus the partition function), and hence the entropy,

$$S = \frac{5}{2}nR + nR\ln\left[\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{3/2}\frac{V g_{e1}}{N_A}\right]$$

increases owing to the term from the partition function for translation. If you refer back to lecture video 1.5,

$$\epsilon_{\mathrm{trans}} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

defines the allowed translational energies for a particle moving in three dimensions, where a, b, and c are the dimensions of a macroscopic box. As you can see, the energy levels are *inversely* proportional to the mass of the atom.

Molecular Thermodynamics
Week 6 Lecture Assessment Questions:

June 23 - June 30, 2013

`Thermo_Vid_06_07`

A) According to the second law of thermodynamics,

  (a) The enthalpy of the universe is tending toward a maximum.

  (b) The enthalpy of the universe is tending toward a minimum.

  (c) The entropy of the universe is tending toward a maximum.

  (d) The entropy of the universe is tending toward a minimum.

Answer:

If we consider any isolated system, we know that for any entropy change in the state of that system,

$$dS \geq \frac{\delta q}{T}$$

For any irreversible process in which the system goes from state 1 to state 2, the entropy change is greater than zero, i.e.,

$$\Delta S = S_2 - S_1 > 0.$$

The universe can be considered an isolated system (were it not, we would simply extend its boundaries to incorporate anything not already included!) As almost all processes that occur naturally are irreversible, the entropy of the universe is constantly increasing. The ultimate maximum is known, colorfully, as "heat death".

Molecular Thermodynamics
Week 6 Lecture Assessment Questions:

June 23 - June 30, 2013

`Thermo_Vid_06_08`

A) For the irreversible adiabatic compression of an ideal gas, the change in entropy of the surroundings is equal in magnitude and opposite in sign to the change in entropy of the system ($\Delta S_{\text{surroundings}} = -\Delta S_{\text{system}}$).

  (a) TRUE

  (b) $\boxed{\text{FALSE}}$

  If a process is adiabatic, no heat is transferred from the system to the surroundings (or vice versa). So, there can be no change in entropy of the surroundings. Note that, since the entropy change of the *universe* for an irreversible process must be greater than zero, the entropy of the gas (the system) must *increase* on compression. As the volume has decreased, it must be the case that the temperature has increased sufficiently to offset the loss of entropy that would otherwise be associated with a volume decrease. Remember the Fire-Starter Piston demonstration?

`Thermo_Vid_07_1`

A) Which of the following expressions is appropriate for dH?

   (a) $dH = SdT - PdV$

   (b) $dH = SdT$

   (c) $dH = TdS$

   (d) $dH = TdS - PdV$

   (e) $\boxed{dH = TdS + VdP}$

   (f) $dH = PdV + SdT$

   (g) $dH = q_{rev} - w_{rev}$

<u>Answer:</u>
We can refer back to the definition of enthalpy given in lecture video 5.7 to see that

$$
\begin{aligned}
H &= U + PV \\
dH &= d(U + PV) \\
dH &= dU + d(PV) \\
dH &= dU + PdV + VdP
\end{aligned}
$$

and now we can substitute $dU = TdS - PdV$ developed in the last lecture slide.

$$
\begin{aligned}
dH &= dU + PdV + VdP \\
dH &= TdS - PdV + PdV + VdP
\end{aligned}
$$

and therefore,

$$
\boxed{dH = TdS + VdP}
$$

`Thermo_Vid_07_2`

A) The entropy of a system can be stated in terms of the probability of being in a given state j as,

(a) $S = k_{\mathrm{B}} \ln \sum_j p_j$

(b) $S = k_{\mathrm{B}} p_j \ln \sum_j p_j$

(c) $S = -k_{\mathrm{B}} \ln \sum_j p_j$

(d) $S = -k_{\mathrm{B}} \sum_j p_j$

(e) $\boxed{S = -k_{\mathrm{B}} \sum_j p_j \ln p_j}$

(f) $S = k_{\mathrm{B}} \sum_j p_j \ln p_j$

Answer:

We can start with the most famous equation of thermodynamics,

$$S = k_B \ln W$$

which was discussed in lecture video 6.4. W is the number of ways of having a_1 systems in state 1, a_2 systems in state 2, and a_3 systems in state 3... for an ensemble of A systems. It was shown in the lecture video that

$$W(a_1, a_2, a_3, \dots) = \frac{A!}{a_1! a_2! a_3! \dots} = \frac{A!}{\Pi_j a_j!}$$

If we substitute this into the equation for entropy above we get for the ensemble

$$S = k_B \ln \frac{A!}{\Pi_j a_j!} = k_B \ln A! - k_B \sum \ln a_j!.$$

If we now apply Stirlings approximation, $\ln N! = N \ln N - N$
,

$$S = k_B A \ln A - k_B A - k_B \sum_j a_j \ln a_j + k_B \sum_j a_j.$$

However, $k_B \sum_j a_j = k_B A$, and thus

$$S = k_B A \ln A - k_B \sum_j a_j \ln a_j.$$

The probability that the system is in quantum state j is

$$p_j = \frac{a_j}{A}$$

Substituting into the above equation,

$$S = k_B A \ln A - k_B \sum_j p_j A \ln(p_j A)$$

$$= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A.$$

Now if we realize that $\sum_j p_j = 1$ and thus the first and last term cancel each other out, which leaves $S = -A k_B \sum_j p_j \ln p_j$. In a large ensemble, the entropy of a given system should be the average of the entropy of the ensemble, so we can divide this expression by the total number of states in the ensemble A, giving $\boxed{S_{sys} = -k_B \sum_j p_j \ln p_j}$

Molecular Thermodynamics
Week 7 Lecture Assessment Questions:

July 1 - July 7, 2013

`Thermo_Vid_07_3`

A) Consider a mole of diatomic molecules at 117 K. The following equation,

$$S = \int_{0\ \text{K}}^{117\ \text{K}} \frac{C_P\, dT}{T}$$

is true for this sample only if:

(a) The sample is ideal

(b) The melting point of the sample is 116 K

(c) $S(0\ \text{K}) = 0$

(d) There are no phase transitions between 0 K and 117 K

(e) The sample is in the Debye T^3 limit over the entire temperature range

(f) The sample is ideal **AND** There are no phase transitions between 0 K and 117 K

(g) $\boxed{S(0\ \text{K}) = 0 \textbf{ AND} \text{ There are no phase transitions between 0 K and 117 K}}$

(h) none of the above

Answer:

This equation applies to all substances, so it is not true that the equation will apply only if the sample is ideal. It can't be true, either, that the equation will apply if the melting point of the substance is 116 K, since it does not apply over a phase transition. It is true that the equation will apply when $S(0\ \text{K}) = 0$, and indeed this is a requirement as otherwise a constant would need to be added for any non-zero entropy at 0 K (which might be present for something that is not a perfect crystal at 0 K). Also it is true that there cannot be any phase transitions between 0 K and 117 K for the equation to apply (otherwise we would need to add the entropy(ies) of transition for the phase change(s)). The sample may likely be in the Debye T^3 range as the temperature approaches 0 K, however, there is no need for the Debye limit to apply throughout the entire temperature range for the equation to be valid. So, the correct answer is the third and fourth options.

Molecular Thermodynamics
Week 7 Lecture Assessment Questions:

July 1 - July 7, 2013

`Thermo_Vid_07_4`

A) Which of the following diatomic gases will have the largest standard molar entropy, $S°$?

   (a) HF

   (b) HCl

   (c) HBr

   (d) $\boxed{\text{HI}}$

   (e) They all have the same standard molar entropy.

<u>Answer:</u>
Recall that entropy increases as the spacing between energy levels decreases (making more levels accessible at a given temperature). For translation, the spacing between energy levels is inversely proportional to mass, and HI has the largest mass, so it will have the largest translational entropy. Recalling the formula for rotational energy levels in a diatomic molecule using the rigid rotor approximation,

$$\epsilon_j = \frac{\hbar^2}{I} J(J+1), \ (J = 1, 2, 3, 4\ldots)$$

we see that the energy level spacing is inversely proportional to the moment of inertia, $I = m_1 R_1^2 + m_2 R_2^2$, so HI will also have the largest moment of inertia (in part because iodine is the heaviest of the halogen atoms listed and in part because HI will also have the longest bond length, although one would have to look up the bond lengths if one did not know that ahead of time). Finally, while vibrations will not contribute much to the entropy at 298 K, it *will* be true that the heavier the halogen, the weaker the bond, the lower the vibrational frequency, the greater the vibrational entropy. Again, without looking up the vibrational frequencies, one would not necessarily know this ahead of time. However, the translational and rotational components will dominate, and HI is the correct choice.

Molecular Thermodynamics
Week 7 Lecture Assessment Questions:

July 1 - July 7, 2013

`Thermo_Vid_07_5`

A) Which one of the following orderings of the standard molar entropies ($S°$) of the three molecules $CH_3Cl(g)$, $CH_2Cl_2(g)$, and $CHCl_3(g)$ is correct?

   (a) $S°(CH_2Cl_2) > S°(CHCl_3) > S°(CH_3Cl)$

   (b) $S°(CHCl_3) < S°(CH_2Cl_2) < S°(CH_3Cl)$

   (c) $\boxed{S°(CH_3Cl) < S°(CH_2Cl_2) < S°(CHCl_3)}$

   (d) $S°(CH_2Cl_2) < S°(CHCl_3) < S°(CH_3Cl)$

   (e) $S°(CH_3Cl) = S°(CH_2Cl_2) < S°(CHCl_3)$

   (f) none of the above

<u>Answer:</u>

Recall that entropy increases as the spacing between energy levels decreases (making more levels accessible at a given temperature). For translation, the spacing between energy levels is inversely proportional to mass, and chloroform ($CHCl_3$) has the largest mass, so it will have the largest translational entropy, followed by dichloromethane (CH_2Cl_2), and chloromethane (CH_3Cl). The heavier halogens will also make the moments of inertia for the molecules increase with increasing halogen substitution, which will lead to the same ordering of rotational entropies. These terms will dominate the overall entropy, so we will not worry about the vibrations in these molecules.
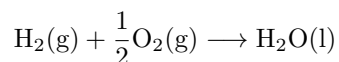
Molecular Thermodynamics
Week 7 Lecture Assessment Questions:

July 1 - July 7, 2013

`Thermo_Vid_07_6`

A) The standard entropy for the reaction

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

is:

(a) positive

(b) negative

(c) equal to zero

Answer:

The reaction involves the conversion of one and one half moles of gases to one mole of liquid. As the number of particles decreases and the relative disorder of the phases also decreases, the entropy change is (strongly) negative.

B) The standard entropy of the reaction for the water shift reaction

$$C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g)$$

is:

(a) positive
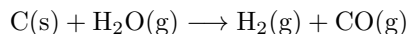
(b) negative

(c) equal to zero

Answer:

In this case, the number of moles of products is equal to the number of moles of reactants, but one equivalent of reactants is a solid (highly ordered) that is converted to a mole of products that is a gas (highly disordered) so that the entropy change is (strongly) positive.

MOOC Week 8 Lecture Assessment

Thermovid_8_01

1. Work and heat are, in general:

   (a) state functions

   (b) $\boxed{\text{path functions}}$

   (c) exact differentials

   (d) intensive variables

   (e) state functions *AND* exact differentials

   (f) path functions *AND* exact differentials

   (g) none of the above

   <u>Answer:</u>

   Work and heat are path functions. The amount of work done by or done on a system, as well as the amount of heat transferred from system to surroundings, or vice versa, are dependent upon the path taken by the system. As a simple example, recall that for the adiabatic expansion of an ideal gas from (P_1, V_1, T_1) to (P_2, V_2, T_2), $q = 0$. However, if the expansion is first done isothermally from (P_1, V_1, T_1) to (P_3, V_2, T_1), and then at constant volume to (P_2, V_2, T_2), $q = nRT \ln \frac{V_2}{V_1} + C_V(T_2 - T_1)$.

   Neither heat nor work can be state functions, except under the special circumstances that one is identically zero, in which case the other, being equal to the state function U, must also be a state function. A state function has the same value regardless of the path taken between the initial state and final state. In addition, by definition, the differential of a state function is exact, meaning that the cross derivatives are equal and the function can be integrated in the normal way, i.e.,

   $$\int_1^2 dx = x_2 - x_1 \quad \text{exact}$$

   $$\int_1^2 dx \neq x_2 - x_1 \quad \text{inexact}$$

   In general, q and w are path functions, and therefore their differentials are inexact.

   Heat and work are extensive quantities. The amount of heat or work associated with a change of state depends on the size of the system. Imagine the isothermal compression of one mole of an ideal gas. If instead *two* moles of gas were compressed equivalently, side by side, twice as much heat would be transferred from the systems to the surroundings.

MOOC Week 8 Lecture Assessment

`Thermovid_8_02`

1. For an ideal gas at constant temperature, which of the following statements is true?

   (a) The Gibbs energy increases when the pressure increases .

   (b) The Gibbs energy decreases when the pressure increases.

   (c) The Gibbs energy does not change when the pressure increases.

   Answer:

   Recall that $\Delta G = \Delta H - T\Delta S$. The change in enthalpy of an ideal gas depends only upon the temperature, so, in the case of constant temperature, $\Delta H = 0$. However, as the gas is compressed, the entropy decreases (so the sign of ΔS is negative), and thus ΔG increases with increasing pressure at constant temperature.

MOOC Week 8 Lecture Assessment

`Thermovid_8_03`

1. We just derived

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

For an ideal gas, what is the value of

$$\left(\frac{\partial U}{\partial V}\right)_T ?$$

(a) RT

(b) $\frac{3}{2}\bar{R}T$

(c) $C_V(T)T$

(d) N_A

(e) $\boxed{0}$

<u>Answer:</u>

We need not do any calculations to answer this question. Recall that the energy of an ideal gas depends only upon its temperature. So, for an isothermal (i.e., constant temperature) process, the change in U must be equal to zero. Of course, one *can* do the calculation. For the ideal gas, $P = nRT/V$, and thus $\left(\frac{\partial P}{\partial T}\right)_V = nR/V$ Inserting these expressions for P and $\left(\frac{\partial P}{\partial T}\right)_V$ in the above expression for $\left(\frac{\partial U}{\partial V}\right)_T$ does indeed lead to a value of zero.

MOOC Week 8 Lecture Assessment

Thermovid_8_04

1. Using Maxwell relations, we derived the following expression,

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

What is the correct expression for $\left(\frac{\partial \bar{H}}{\partial P}\right)_T$ for a gas that obeys the following equation of state?

$$P\bar{V} = RT + B(T)P$$

where $B(T)$ is a temperature dependent coefficient.

(a) $\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \bar{V} - T\left(\frac{dB}{dT}\right)$

(b) $\boxed{\left(\frac{\partial \bar{H}}{\partial P}\right)_T = B(T) - T\left(\frac{dB}{dT}\right)}$

(c) $\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \frac{RT}{P} - \frac{RT}{P}\left(\frac{dB}{dT}\right)$

(d) $\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \frac{RT}{P} - B(T)$

(e) $\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \frac{RT}{P}B(T) - \frac{RT}{P}\left(\frac{dB}{dT}\right)$

Answer:

We answer this question by solving for the molar volume and its derivative with respect to temperature and then substituting those values into the expression for $\left(\frac{\partial \bar{H}}{\partial P}\right)_T$:

$$\bar{V} = \frac{RT}{P} + B(T),$$

therefore,

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{P} + \left(\frac{dB}{dT}\right).$$

After substitution,

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \frac{RT}{P} + B(T) - T\left[\frac{R}{P} + \left(\frac{dB}{dT}\right)\right]$$

$$= B(T) - T\left(\frac{dB}{dT}\right)$$

MOOC Week 8 Lecture Assessment

`Thermovid_8_05`

1. If the ideal rubber band is stretched adiabatically, what is the change in internal energy, ΔU.

   (a) δq

   (b) RT

   (c) fdS

   (d) 0

   (e) $\boxed{fdl}$

   Answer:

   We know from the previous slide that

   $$dw = fdl - PdV.$$

   If the rubber band is stretched adiabatically, then $q = 0$; therefore

   $$\Delta U = q + w = 0 + fdl - PdV.$$

   As was mentioned in this lecture video, the volume change upon stretching is negligible, therefore

   $$\Delta U = fdl.$$

MOOC Week 8 Lecture Assessment

`Thermovid_8_06`

1. Which of the following is the correct expression for the Helmholtz energy in terms of its natural independent variables?

   (a) $dA = PdS - TdV$

   (b) $dA = TdS + VdP$

   (c) $dA = -SdT + VdP$

   (d) $dA = TdS - PdV$

   (e) $\boxed{dA = -SdT - PdV}$

   <u>Answer:</u>

   The Helmholtz thermodynamic state function is defined,

   $A = U - TS$ and thus $dA = dU - d(TS) = dU - TdS - SdT$. However, we know that for any reversible process (recall that we can define the change in U, a state function, along any path), $dU = TdS - PdV$. So we substitute to get,

   $$
   \begin{aligned}
   dA &= dU - d(TS) = dU - TdS - SdT \\
   &= TdS - PdV - TdS - SdT \\
   &= -SdT - PdV
   \end{aligned}
   $$

2. (pts) Using the first and second laws of thermodynamics, dU can be expressed in terms of its natural independent variables as:

(a) $dU = SdT + VdP$

(b) $dU = SdT - VdP$

(c) $dU = TdS + VdP$

(d) $\boxed{dU = TdS - PdV}$

(e) $dU = TdS + PdV$

(f) $dU = SdT + PdV$

(g) $dU = SdT - PdV$

(h) none of the above

Answer:

We know from the week 5 series of lecture videos that

$$dU = \delta q + \delta w.$$

Since U is a state function we can evaluate the change in U along any path. A convenient path to choose is a reversible path, therefore

$$dU = \delta q_{\text{rev}} + \delta w_{\text{rev}}.$$

From the definition of reversible work we know $dw_{\text{rev}} = -PdV$ and from the second law that $\delta q_{\text{rev}} = TdS$. Substituting into the equation above,

$$dU = TdS - PdV.$$

S and V are therefore the natural independent variables of U, which means that the total derivative of U takes on a simple form. In other words, from

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

we see that the coefficients of the dS and dV are the simple thermodynamic functions T and P. Here $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$.

MOOC Week 8 Lecture Assessment

`Thermovid_8_07`

1. Using Maxwell relationships, we derived the following expression for the change in the Gibbs energy as function of pressure at constant temperature for an ideal gas,

$$\Delta \bar{G} = RT \ln \frac{P_2}{P_1}.$$

    If temperature is held constant, the change in Gibbs energy with pressure is due to the,

    (a) | change in the entropy with pressure. |

    (b) change in the enthalpy with pressure.

    (c) the change in both the entropy and enthalpy with temperature.

    (d) change in the heat capacity with pressure.

    (e) none of the above

    In this weeks lecture videos, we learned that,

    $$G = H - TS$$

    and at constant temperature
    $$\Delta G = \Delta H - T\Delta S$$

    and we discussed in week 5, the enthalpy of an ideal gas depends only on temperature, and thus ΔH is zero for an isothermal process involving an ideal gas. So, the change in the free energy, ΔG, must be due solely to the change in entropy, ΔS.