CHEM2011 office hours notes

Jerry Wu

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Test 1 notes

Terminology and cases

- **Isothermal** $\implies T \equiv const \implies q = -w = -nRT\ln(\frac{V_2}{V_1}) = -nRT\ln(\frac{P_1}{P_2}), \Delta U = \Delta H = 0$
- **Isobaric** $\implies P \equiv const \implies w = P\Delta V, \Delta V > 0 \implies expansion, \Delta V < 0 \implies compression, \Delta H = q$
- **Isochoric** $\implies V \equiv const \implies w = 0, \Delta U = q, \Delta H = \Delta U + V\Delta P$
- **Adiabatic** $\implies q = 0 \implies \Delta U = w \implies T_1 P_1^{\frac{1-\gamma}{\gamma}} = T_2 P_2^{\frac{1-\gamma}{\gamma}}, \Delta H = 0$

Definition of a state function and constants

- A function $f(x,y)$ is a state function if and only if the following property is satisfied::

$$\left(\frac{\left(\frac{\partial f}{\partial x}\right)_y}{\partial y}\right)_x = \left(\frac{\left(\frac{\partial f}{\partial x}\right)_y}{\partial y}\right)_x$$

- For monoatomic gases, $\bar{C_V} = \frac{3}{2}R$, $\bar{C_P} = \frac{5}{2}R$, $\gamma = \frac{\bar{C_P}}{\bar{C_V}} = \frac{5}{3}$
- For diatomic gases (assume no vib.),$\bar{C_V} = \frac{5}{2}R$, $\bar{C_P} = \frac{7}{2}R$, $\gamma = \frac{\bar{C_P}}{\bar{C_V}} = \frac{7}{5}$
- The cyclic rule for enthalpy $H(T,P)$ is defined as the following::

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

Practice test questions

Question 1

a) Briefly answer the following:

  i) Does Charles' Law hold during a reversible adiabatic expansion or compression of an ideal gas? Briefly explain your answer.

  Answer:: No, Charles' law will not hold for an adiabatic expansion because $P \equiv const$ must be true. In adiabatic expansion and compression, $\neg P \equiv const$.

  ii) (T/F) Dalton's Law of partial pressure states that for unreactive gases, behaving ideally, the pressure exerted by one gas in a mixture is independent of the other gases in the mixture.

  Answer:: This is true, because partial pressures in a gas mixture are independent of one another.

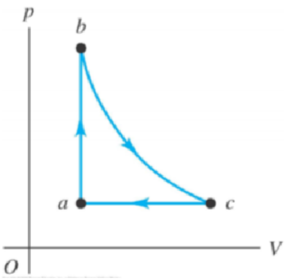
  iii) (T/F) For real gases the ratio $\frac{PV}{RT}$ can be greater or smaller than one. A positive deviation (meaning $\frac{PV}{RT} > 1$) is due to the molecules having intermolecular forces and is quantified by the a factor.

  Answer:: This is false. Looking at the Van der Waals equation, we can see that the a value is in the numerator.

  iv) (T/F) Non-ideal behavior in gases is more important at high temperature and low pressure.

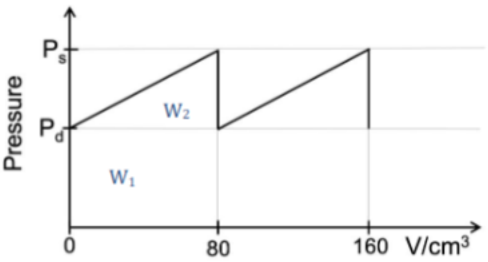
  Answer:: False

  v) An ideal gas is taken around the cycle (a-b-c-a) shown in this PV–diagram. Process $b \to c$ is isothermal. For the complete cycle, what are the signs of q, w and ΔU positive, negative or zero?



Answer:: The process is isothermal, so clearly $\Delta U = 0$ must be immediately true. From here, we can look at the PV diagram to determine the signs of q and w. Here we can see that in process $b \to c$, pressure decreases as the volume increases. From this, we can say that $w < 0$ due to the process being an expansion. So clearly $q > 0$ must be true for the process as well.

b) The PV diagram below can be used to represent the pressure dependence in a ventricle of the human heart as a function of the volume of blood pumped. The systolic pressure, P_s, is $137mmHg$, and the diastolic pressure P_d, is $81mmHg$. If the volume of blood pumped in one heartbeat is $80cm^3$, calculate the work done in one heartbeat.



Answer::

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

Since there is no curve, we can simply calculate work as the area of a rectangle and triangle for P_s and P_d respectively.

$$w_1 = P_d(V_2 - V_1) = (\frac{81torr}{760torr})101325Pa(80E - 6m^3 - 0) = 0.8639J$$

$$w_2 = \frac{bh}{2} = \frac{(P_s - P_d)(V_2 - V_1)}{2} = \frac{\frac{56torr}{760torr}101325Pa(80E - 6m^3)}{2} = 0.2986J$$

Now we can add our values of work together for one heartbeat.

$$w = \sum_{\Omega} w_i = 0.2986J + 0.8639J = 1.163J \approx 1.2J$$

$\therefore$ each heartbeat does around 1.2J of work.

Question 2

a) A $243.0g$ sample of Silicon (Si) in the **crystalline solid form** is heated from $300K$ to $425K$ at **constant pressure**. Over this temperature range, $C_{P,m}$ is given by the expression:

$$\frac{C_{P,m}}{JK^{-1}mol^{-1}} = -6.25 + 0.1681\frac{T}{K} - (3.437E - 4)\frac{T^2}{K^2}$$

Calculate ΔH and q_P.

Answer::

Because we are given $C_{P,m}$ as a function of T, we can use the definition of ΔH for an ideal gas.

$$\forall g \in \mathbb{C}, \Delta H = n \int_{T_1}^{T_2} C_{P,m} dT$$

$$\Delta H = \frac{243.0g}{28.0855gmol^{-1}} \int_{300K}^{425K} \left(-6.25 + 0.1681\frac{T}{K} - (3.437E - 4)\frac{T^2}{K^2}\right) dT$$

Integrating the polynomial with respect to T, we have that::

$$\Delta H = \frac{243.0g}{28.0855gmol^{-1}}\left(-6.25T + \frac{0.1681}{2}T^2 - \frac{3.437E-4}{3}T^3\right)$$

So now, we can plug in our values of T_2 and T_1 to calculate our ΔH.

$$\Delta H = \frac{243.0g}{28.0855gmol^{-1}}\times$$

$$\left(-6.25(425-300) + \frac{0.1681}{2}(425^2-300^2) - \frac{3.437E-4}{3}(425^3-300^3)\right)$$

After a long and tedious calculation, we have found our value for ΔH

$$\Delta H = 8.652(-781.25 + 7617 - 5701.5) = 9814J \approx 9.81kJ$$

We do not have to calculate q_P, because $P \equiv const \implies \Delta H = q_P$

b) How large is the relative error in ΔH if we assume that $C_{P,m}$ is a constant at $300K$ and that $C_{P,m}$ remains constant for temperature interval considered in part (a)?

Answer::

We can simply evaluate $C_{P,m}(T = 300K)$ to find our ΔH when temperature is constant.

$$C_{P,m}(300) = -6.25 + 0.1681(300) - (3.437E-4)(300) = 13.247JK^{-1}mol^{-1}$$

$$\Delta H = nC_{P,m}\Delta T = \frac{243.0g}{28.0855gmol^{-1}}13.247(425-300) = 14.3kJ$$

So now we can calculate relative error.

$$\%Err_{relative} = \frac{9.81-14.3}{9.81}\times 100\% \approx \pm 46\%$$

c) For the process described in part (a) calculate ΔU.

Answer::

A calculation is not required for this section. This is because $\forall solids, \Delta U \approx \Delta H$

Question 3

A sample of **two moles** of an **ideal diatomic gas** is initially at **T = 290K** and at a pressure of **10.0 bar**.

a) The gas then undergoes a **reversible adiabatic expansion** to a final pressure of $1.50 bar$. Calculate T_f, q, w, ΔU, and ΔH.

Answer::

First off, the process is an adiabatic expansion, so clearly $q = 0$.

For diatomic gas molecules, we have the following heat capacities an constants::

$$C_{P,m} = \frac{7}{2}R, C_{V,m} = \frac{5}{2}R, \gamma = \frac{7}{5}$$

We can use the following equation to find the value of T_2.

$$T_1 P_1^{\frac{1-\gamma}{\gamma}} = T_2 P_2^{\frac{1-\gamma}{\gamma}} \implies T_2 = \frac{T_1 P_1^{\frac{1-\gamma}{\gamma}}}{P_2^{\frac{1-\gamma}{\gamma}}} = T_1 \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}} = 290 \left(\frac{10}{1.5}\right)^{\frac{1-\frac{7}{5}}{\frac{7}{5}}} = 169K$$

From here, our job is to find the values of ΔU and ΔH, since we know that $\Delta U = w$ in an adiabatic process.

$$\Delta U = w = C_V(T_2 - T_1) = \frac{5}{2}\left(8.314\frac{J}{Kmol}\right)(2mol)(169 - 290) \approx -5.03kJ$$

$$\Delta H = C_P(T_2 - T_1) = \frac{7}{2}\left(8.314\frac{J}{Kmol}\right)(2mol)(169 - 290) \approx -7.04kJ$$

b) In a second experiment, the gas sample is found at the same initial conditions, but it expands to a **final pressure** of $1.50 bar$ during an **irreversible adiabatic expansion** against a **constant pressure** of $1.50 bar$, calculate the final temperature and the work done in that process.

Answer::

To find T_2, we can apply the following formula and rearrange as needed::

$$nC_{V,m}(T_2 - T_1) = -P_{ext}(V_2 - V_1) \implies nC_{V,m} = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

Rearranging the equation, we have that

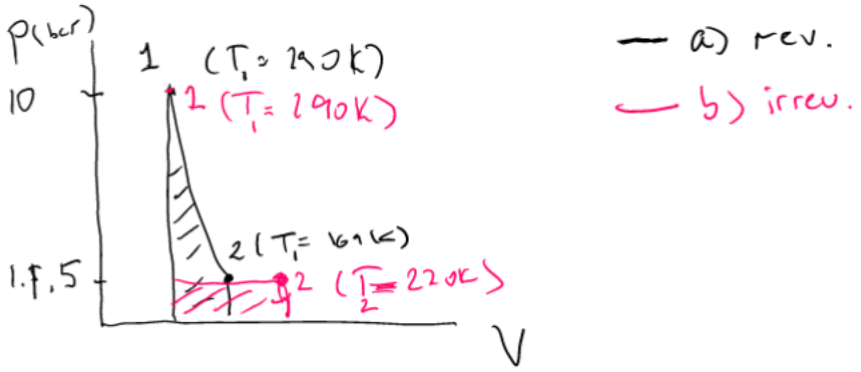
$$\left(C_{V,m} + \frac{RP_{ext}}{P_2}\right)T_2 = \left(C_{V,m} + \frac{RP_{ext}}{P_1}\right)T_1 \implies T_2 = \frac{\left(C_{V,m} + \frac{RP_{ext}}{P_1}\right)T_1}{\left(C_{V,m} + \frac{RP_{ext}}{P_2}\right)}$$

$$T_2 = \frac{\left(\frac{5}{2} + \frac{1.5bar}{10.0bar}\right)}{\left(\frac{5}{2} + \frac{1.5bar}{1.5bar}\right)}(290K) \approx 220K$$

Here, $P_2 = P_{ext}$ because the process is an irreversible expansion.
Finally, we calculate our ΔU.

$$\Delta U = w = C_V(T_2 - T_1) = \frac{5}{2}(8.314JK^{-1}mol^{-1})(2mol)(220K - 290K) \approx -2.91kJ$$

c) On the same PV diagram, sketch the work that was done in a) as well as in b). Clearly label the area that corresponds to each of the processes. Who did the work in a) and b) the system or the surroundings?



Since $w < 0$ for both a) and b), we can conclude that work is done by the surroundings.

Question 4

a) Enthalpy (H) is a state function and dH is an exact differential. Write an expression for the full differential expression of dH illustrating the dependence of enthalpy on P and T.

Answer::

The full differential can be expressed as the following sum of partial derivatives::

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

b) Write the cyclic rule expression for $H(T, P)$

Answer::

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

c) Prove that $\forall g \in \mathbb{C}, \left(\frac{\partial H}{\partial P}\right)_T = 0$

Answer::

We can begin by using the following identity::

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

We can substitute $P = \frac{nRT}{V}$ and $V = \frac{nRT}{P}$ to differentiate.

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial\left(\frac{nRT}{V}\right)}{\partial T}\right)_V = \frac{nR}{V}$$

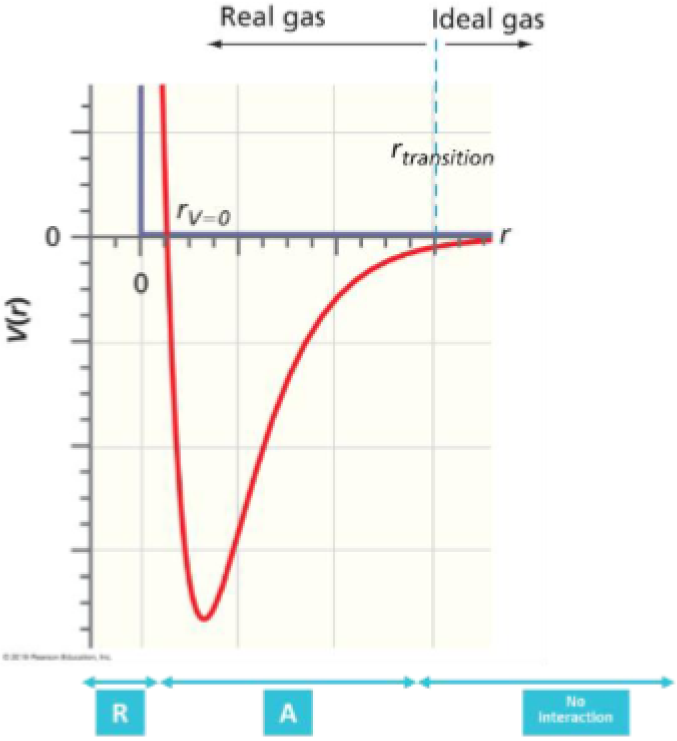
$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial P}\right)_T = -\frac{1}{P^2}nRT = -\frac{nRT}{P^2}$$

So now, we can substitute these values back into the original equation.

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T + V = T\frac{nR}{V}\left(-\frac{nRT}{P^2}\right) + V = 0\blacksquare$$

d) The potential energy of interaction of two molecules or atoms is shown in the figure below (as a function of their separation, r). On the diagram, indicate where there is i) no interaction, ii) attraction, iii) repulsion between gas molecules.

Answer::



iv) $\forall g \in \mathbb{R}$, $\left(\frac{\partial H}{\partial P}\right)_T = -C_P\mu_{J-T}$. In which region is $\left(\frac{\partial H}{\partial P}\right)_T > 0$ for real gases?
Answer:: The repulsive region.