Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 03
Tutorial - 01

In this lecture, we will discuss the applications of the concept that we developed in the previous lecture. In the previous lecture, we talked about work, and derived several equations. And let us see how to use those equations to calculate the work under different conditions. So, we will discuss a few numerical problems; and if there are any questions, queries at any step, please keep on writing, and then let us know where you could not understand.

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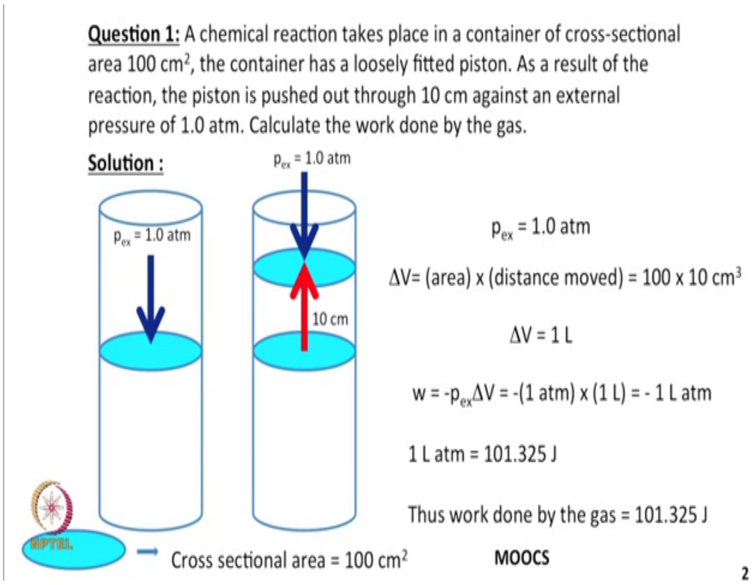

Question 1: A chemical reaction takes place in a container of cross-sectional area 100 cm^2, the container has a loosely fitted piston. As a result of the reaction, the piston is pushed out through 10 cm against an external pressure of 1.0 atm. Calculate the work done by the gas.

Solution :

p_{ex} = 1.0 atm

ΔV= (area) x (distance moved) = 100 x 10 cm^3

ΔV = 1 L

$w = -p_{ex}\Delta V$ = -(1 atm) x (1 L) = - 1 L atm

1 L atm = 101.325 J

Thus work done by the gas = 101.325 J

MOOCS

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Let us consider this question number 1, which is a chemical reaction, takes place in a container of cross sectional area 100 centimeter square. The container has loosely fitted piston. As a result of the reaction, the piston is pushed out through 10 centimeter against an external pressure of 1 atmosphere. Calculate the work done by the gas. And it is a very simple problem. As you can see in this figure that you have a container with a cross sectional area of 100 centimeter square; and the piston is moved out or moved upwards by 10 centimeter. And what we have to do is to calculate the work done by the gas. So, how do we approach this question? First, let us try to identify whether the conditions given to us are reversible or irreversible. Please note that the piston is pushed out against an external pressure of one atmosphere the external pressure is fixed, therefore, the process is irreversible; it is not reversible.

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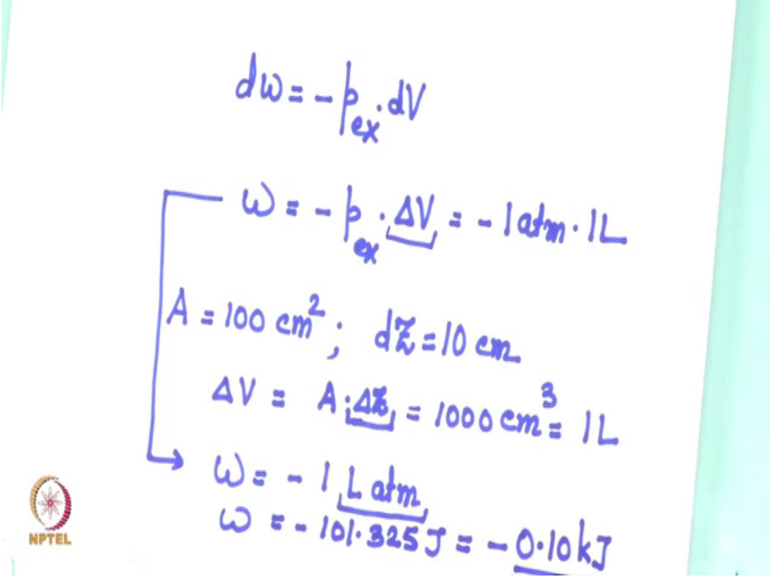

$$dw = -p_{ex} \cdot dV$$

$$w = -p_{ex} \cdot \underbrace{\Delta V} = -1\,atm \cdot 1L$$

$$A = 100\,cm^2 ; \quad dZ = 10\,cm$$

$$\Delta V = A \cdot \underbrace{\Delta Z} = 1000\,cm^3 = 1L$$

$$w = -1\,\underbrace{L\,atm}$$

$$w = -101.325\,J = -\underline{0.10\,kJ}$$

So, therefore, we use this equation dw is minus p external times dV or you take the integrated form of this minus p external times delta V; delta V is V final minus V initial. And in the given problem, you have the area, area of cross section as 100 centimeter square, and the length moved dZ is equal to 10 centimeters. Therefore, the change in volume delta V will be equal to area into whatever is the distance moved which is equal to 1000 centimeter cube - 100 into 10 - 1000 centimeter cube which is equal to 1 liter. So, now we substitute into this that is equal to minus 1 atmosphere into 1 liter. So, the work done is equal to minus 1 liter atmosphere.

Now, if you look into this slide the same thing is shown over there that is delta V which is equal to area times distance moved turns out to be 1 liter and the work done is 1 liter atmosphere. Liter atmosphere can also be used as a unit of work, but it is better to use Joules. And please note the conversion factor; 1 liter atmosphere is equal to 101.325 Joules. So, therefore, in order to convert liter atmosphere into Joules what I will do is I will multiply by a factor of 101.325. And if I multiply by a factor of 101.325, the work done will be equal to minus 101.325 Joules, and this is equal to minus 0.10 kilo Joules.

Please note that the sign is negative. You know in thermodynamics, let us not just go by the numbers, numbers have certain meaning, but in addition to the number, the sign also has a lot of meaning. Negative sign means you remember that I pack signs and conventions, negative means something has left the system. And here the negative can it has to be interpreted in the sense that the work has been done by the gas, work has been done by the system, and this work is done to push back the piston into the surroundings.

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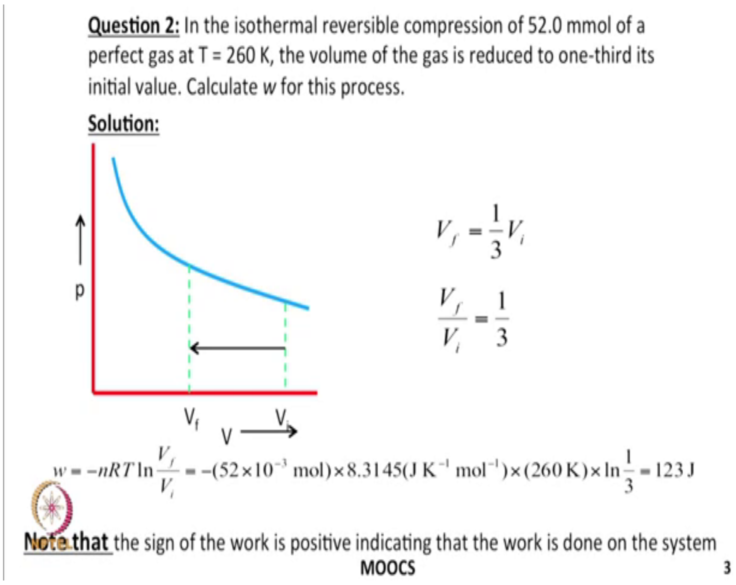

Question 2: In the isothermal reversible compression of 52.0 mmol of a perfect gas at T = 260 K, the volume of the gas is reduced to one-third its initial value. Calculate *w* for this process.

Solution:

$$V_f = \frac{1}{3}V_i$$

$$\frac{V_f}{V_i} = \frac{1}{3}$$

$$w = -nRT\ln\frac{V_f}{V_i} = -(52\times10^{-3}\ \mathrm{mol})\times8.3145(\mathrm{J\ K^{-1}\ mol^{-1}})\times(260\ \mathrm{K})\times\ln\frac{1}{3} = 123\ \mathrm{J}$$

Note that the sign of the work is positive indicating that the work is done on the system

MOOCS

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Now, let us take another problem of a different kind. From irreversible to let us now discuss in the reversible case. Question number 2, in the isothermal reversible compression of 52 millimol of a perfect gas at 260 Kelvin the volume of the gas is reduced to one-third its initial value, calculate work for this process. So, what do we need to note before we begin answering this question?

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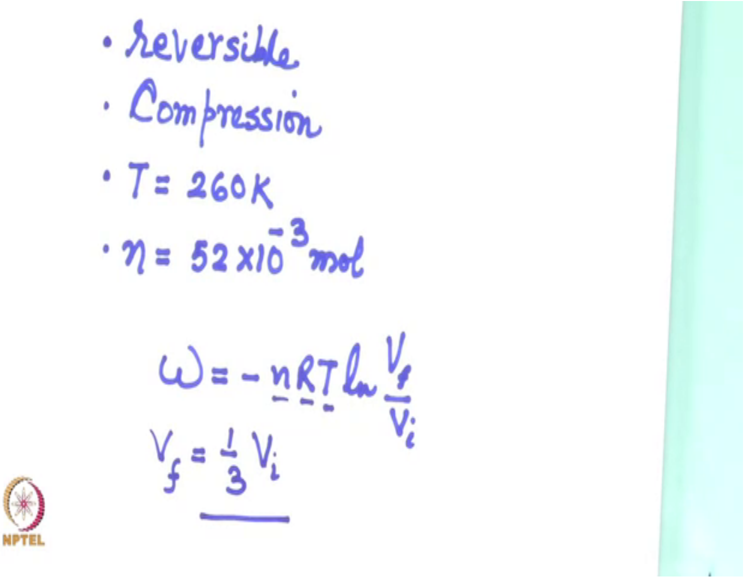

- reversible
- Compression
- $T = 260 K$
- $n = 52 \times 10^{-3} mol$

$$w = -\underline{n}\,\underline{R}\,\underline{T} \ln \frac{V_f}{V_i}$$

$$\underline{V_f = \frac{1}{3} V_i}$$

We note that the process is reversible; and the second thing we note it is compression. And the third thing to note that temperature remains constant, it is isothermal which is 260 Kelvin and then we are given the number of moles which is equal to 52 millimole that is 52 into 10 raise to the power minus 3 mole, this is the given information. Now, we have to use this information to solve the question. It is a reversible compression and when it comes to the compression or expansion of a gas then immediately isothermal reversible pressure volume change of a perfect gas, we can straightaway think of this formula w is equal to minus n R T log V final over V initial. And you see we have the value of n, we have the value of R, we have the value of T what we need to identify what is the ratio of V f to V i. And that information is also given that the volume of the gas is reduced to one-third its initial value that means, final volume is equal to one-third of initial volume.

Now, let us take a look at the slide. We are talking about going from some initial volume to some final volume final volume is lesser than the initial volume which is one by third of V i. So, V f by V i is equal to 1 by 3 and that is what we substitute into the formula minus n R T log V final over V initial. And whenever you are solving the numerical problems, please take care of the units solving the problems in physical chemistry and specifically when I talk about the thermodynamics, you have to use the appropriate units, because units can make a lot of difference if you use the wrong units, you will get incorrect results.

So, here n is 52 into 10 raise to the power minus 3 mol. And I will use the value of R in Joules per Kelvin per mol which is 8.3145, and temperature is 260 Kelvin and then you use log 1 by 3. And after taking care of the units the value of the work which comes out is 123 Joules. Once again the point to be noted here is that the overall sign is positive, and positive sign means that the work is done on the system when you compress the gas, the work is done on the gas, therefore w is equal to plus 123 Joule.

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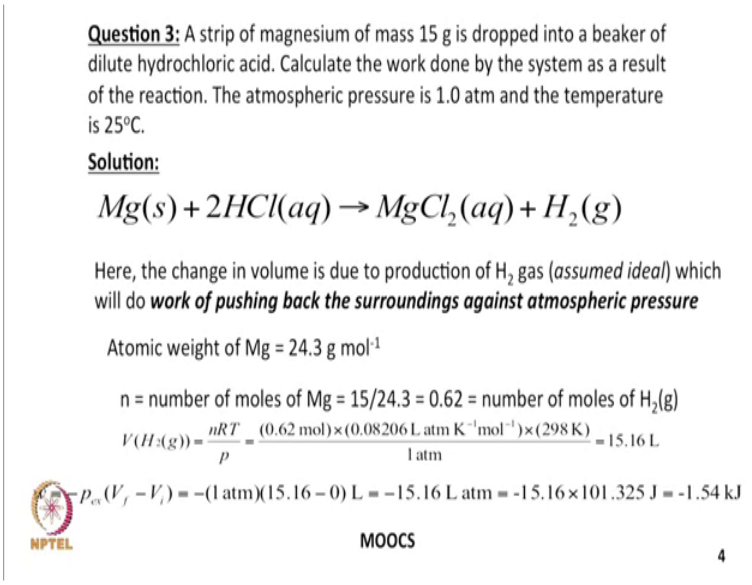

Question 3: A strip of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.0 atm and the temperature is 25°C.

Solution:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Here, the change in volume is due to production of H_2 gas (*assumed ideal*) which will do ***work of pushing back the surroundings against atmospheric pressure***

Atomic weight of Mg = 24.3 g mol^{-1}

n = number of moles of Mg = 15/24.3 = 0.62 = number of moles of $H_2(g)$

$$V(H_2(g)) = \frac{nRT}{p} = \frac{(0.62\ \text{mol}) \times (0.08206\ \text{L atm K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})}{1\ \text{atm}} = 15.16\ \text{L}$$

$$= -p_{ex}(V_f - V_i) = -(1\ \text{atm})(15.16 - 0)\ \text{L} = -15.16\ \text{L atm} = -15.16 \times 101.325\ \text{J} = -1.54\ \text{kJ}$$

MOOCS

Now, let us move onto another problem. Question 3, a strip of magnesium of mass 15 grams is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1 atmosphere, and the temperature is 25 degree Celsius. So, once again let us try to find out the information that is given and which we can make use of. We have here magnesium 15 gram of width is dropped into HCl.

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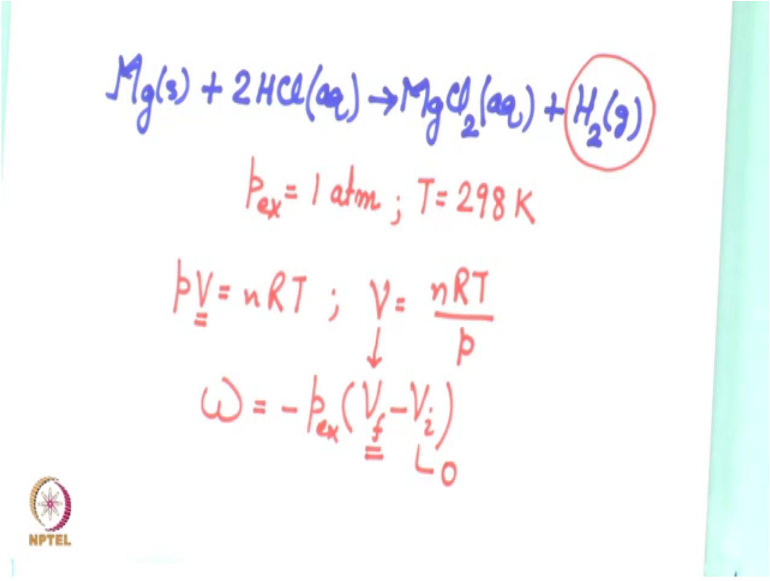

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + \boxed{H_2(g)}$$

$$p_{ex} = 1 \text{ atm} \; ; \; T = 298 \text{ K}$$

$$p\underline{\underline{V}} = nRT \; ; \; \underset{\downarrow}{V} = \frac{nRT}{p}$$

$$\omega = -p_{ex}(\underline{\underline{V_f}} - \underset{\llcorner 0}{V_i})$$

So, work is done due to what, let us see what happens. You have magnesium solid and you add 2 HCl what you get is magnesium chloride plus hydrogen gas. So, it is this hydrogen gas which will drive back the surroundings and work will be done. And solving this problem, we will assume that the hydrogen gas is behaving ideally that is an assumption over here. Now, here again the another point to note is that the atmospheric pressure is 1 atmosphere that means, the p external here is equal to 1 atmosphere that is fixed. Therefore, the process is going to be irreversible and the other information given to you is T is equal to 298 Kelvin - 25 degree centigrade.

So, let us take look at the slide. According to this reaction, the change in volume is due to production of hydrogen gas which we are assuming ideal as I just described. And this gas which will do the work of pushing back the surroundings against atmospheric pressure. So, how do we solve this question? Now, we need the volume of the gas. How do we get the volume of the gas? If we assume this as an ideal gas then we can use the ideal gas equation p V is equal to n R T, and the volume is equal to n R T by p.

So, let us go back to the slide as we can see there, n which is the number of moles of magnesium which is equal to weight divided by the atomic weight - 15 divided by 24.3, it is 0.62. And then if you look at the reaction 1 mole of magnesium produces 1 mole of hydrogen; that means, the number of moles of hydrogen gas produced is also 0.62. And then we substitute this information in the expression for volume, volume is equal to n R

T by p, n is 0.62 mole, R is 0.08206 liter atmosphere per Kelvin per mole, temperature is 298 Kelvin, and pressure is 1 atmosphere. You must be wondering here that why I use R is equal to 8.3145 Joules per Kelvin per mole in the previous question, and here I am using R as 0.08206 liter atmosphere per Kelvin per mole, this is because the pressure given here is in atmosphere.

So, therefore, it will be easier for me to solve this question, if I use the value of R in liter atmosphere per Kelvin per mole. So, the calculation suggests that the volume is 15.16 liter. Now, how do you calculate the work? As usual that work in an irreversible process is minus p external into V f minus V i. V f, this is V f because this volume is due to hydrogen gas produced and initially the gas was not there. Therefore, V i the value I have to set to 0.

Going back to the slide in the last line w is equal to minus p external into V f minus V i and then you use the values 1 atmosphere and 15.16 liter what you get is 15 minus 15.16 liter atmosphere. And once you convert this into Joules by multiplying by 101.325 the final value is minus 1.54 kilo Joules. And once again let us appreciate the meaning of negative value negative value means the work is done by the system and obviously, the work is here done by hydrogen gas as mentioned there that it does the work of pushing back the surrounding against the atmospheric pressure.

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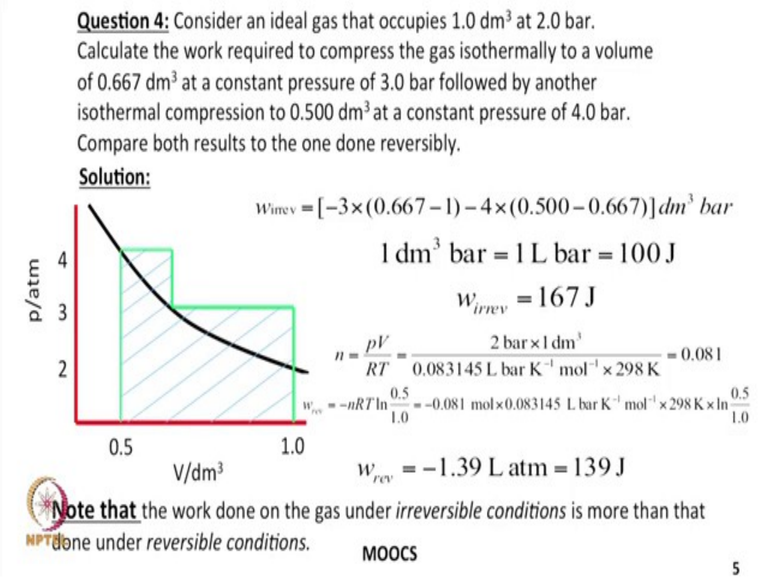

Question 4: Consider an ideal gas that occupies 1.0 dm^3 at 2.0 bar. Calculate the work required to compress the gas isothermally to a volume of 0.667 dm^3 at a constant pressure of 3.0 bar followed by another isothermal compression to 0.500 dm^3 at a constant pressure of 4.0 bar. Compare both results to the one done reversibly.

Solution:

$$w_{irrev} = [-3\times(0.667-1)-4\times(0.500-0.667)]\,dm^3\ bar$$

$$1\ \mathrm{dm^3\ bar} = 1\ \mathrm{L\ bar} = 100\ \mathrm{J}$$

$$w_{irrev} = 167\ \mathrm{J}$$

$$n = \frac{pV}{RT} = \frac{2\ \mathrm{bar}\times 1\ \mathrm{dm^3}}{0.083145\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}\times 298\ \mathrm{K}} = 0.081$$

$$w_{rev} = -nRT\ln\frac{0.5}{1.0} = -0.081\ \mathrm{mol}\times 0.083145\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}\times 298\ \mathrm{K}\times\ln\frac{0.5}{1.0}$$

$$w_{rev} = -1.39\ \mathrm{L\ atm} = 139\ \mathrm{J}$$

Note that the work done on the gas under *irreversible conditions* is more than that done under *reversible conditions.*

Now, let us move to another type of question. Question number 4, consider an ideal gas that occupies 1 decimeter cube at 2 bar. Calculate the work required to compress the gas isothermally to a volume of 0.667 decimeter cube at a constant pressure of 3 bar followed by another isothermal compression to 0.5 decimeter cube at a constant pressure of 4 bar, compare both the results to the one done reversible. So, how do we solve this question, the information given is very clear. The only difference is that instead of liter, the information is given in decimeter cube; and 1 decimeter cube is equal to 1 liter, and the pressure is given in bar. So, this will allow us to look at what is the conversion factor for converting liter bar to Joules, here the gas is again ideal.

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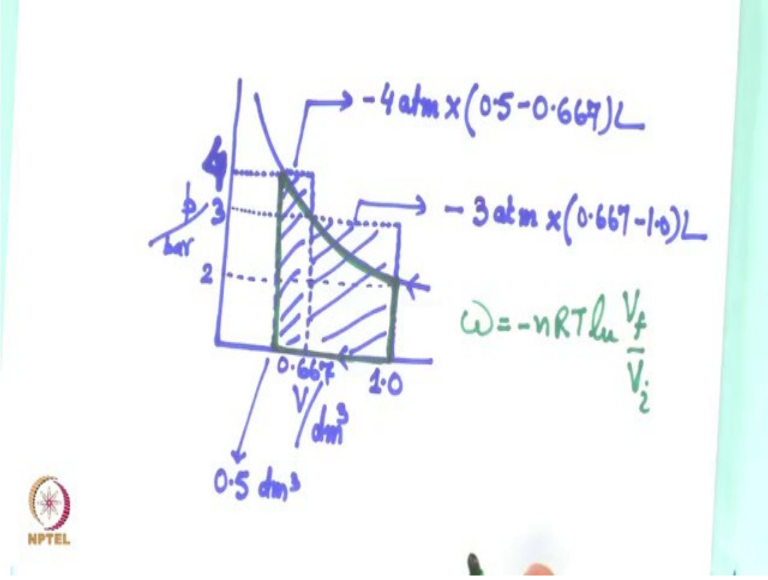

So, when we are talking about the work done in the case of pressure-volume changes in the gas - ideal gas, it makes a sense to immediately draw this kind of diagram. And it is a compression that means, the initial volume let us say this initial volume, this is 1 decimeter cube let me put this in decimeter cube, and the corresponding pressure is 2 bar. In the first step, it is isothermally compressed to 0.667 centimeter cube against a constant pressure of 3 bar; and let us say I put this as 3 bar, and this value is 0.667. And since it is a constant pressure; that means, the work done will be given by this, it is a compression. And then in the second step, it is now compressed to 0.5 decimeter cube against the pressure of 3 bar. Now, let us say if I put this as the 3 bar, this is 3, sorry this is 4, and this is 3. So, this volume is 0.5 decimeter cube and the additional work done is here.

So, we need to add these indicator diagrams to calculate the total work done. So, for this step, the value will be minus p external, p external is equal to 3 atmosphere into it is going to be 0.667 minus 1.0 liter. And this one is going to be minus 4 atmosphere into 0.5 minus 0.667 liter, and the total work done will be the addition of both. Let us take a look at the slide. Now the total irreversible work done by the method that I just described over here after converting the decimeter cube into bar decimeter cube is liter. So, one little bar is equal to 100 Joules, and dissolves to w equal to 167 Joules. So, this work plus this work when you add these two works - these two areas, this gives you a value of 167 Joule.

Now, it says compare both the results to the one done reversibility. Reversibly means now let us say the whole compression is done reversibly that means, we need to talk about the area that I am talk that I am highlighting over here. Either you talk in terms of area or you simply use w is equal to minus n R T log V final over V initial; and V final here is 0.5 and V initial here is 1. And going back to the slide, we need the value of n - number of moles which can be easily calculated from the given information because it is given that the gas occupies 1 liter at 2 bar. So, you use this information and use p V is equal to n R T to get the value of n which turns out to be 0.081. And then when you substitute into w is equal to minus n R T log V final over V initial the number that you get is 139 Joules. Again please note that it is positive.

And if the process were carried out irreversibly, the value was 167 Joules. Now, the process is carried out reversibly, it is 139 Joule. So, irreversible work of 167 Joule which is done on the system is more than the work done on the gas under reversible condition that is 139 Joule. And this is consistent with the discussion that we had that when the gas is compressed more work is done under irreversible conditions then that done under reversible conditions. And that is the conclusion written here on the slide that, note that the work done on the gas under irreversible condition it is more than that than under reversible conditions.

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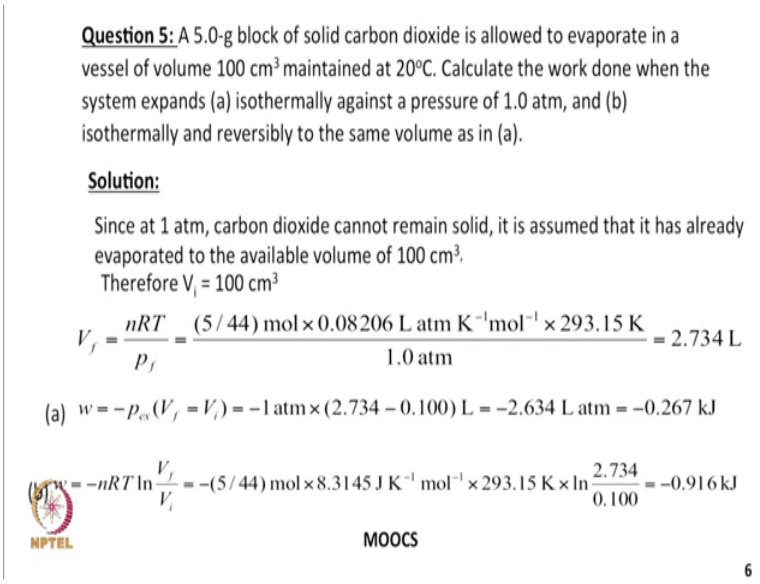

Question 5: A 5.0-g block of solid carbon dioxide is allowed to evaporate in a vessel of volume 100 cm^3 maintained at 20°C. Calculate the work done when the system expands (a) isothermally against a pressure of 1.0 atm, and (b) isothermally and reversibly to the same volume as in (a).

Solution:

Since at 1 atm, carbon dioxide cannot remain solid, it is assumed that it has already evaporated to the available volume of 100 cm^3.

Therefore $V_i = 100$ cm^3

$$V_f = \frac{nRT}{p_f} = \frac{(5/44)\,\text{mol} \times 0.08206\ \text{L atm K}^{-1}\text{mol}^{-1} \times 293.15\ \text{K}}{1.0\ \text{atm}} = 2.734\ \text{L}$$

(a) $w = -p_{ex}(V_f = V_i) = -1\ \text{atm} \times (2.734 - 0.100)\ \text{L} = -2.634\ \text{L atm} = -0.267\ \text{kJ}$

(b) $w = -nRT \ln\frac{V_f}{V_i} = -(5/44)\,\text{mol} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times 293.15\ \text{K} \times \ln\frac{2.734}{0.100} = -0.916\ \text{kJ}$

Now, let us take a look at another type of question. Here the question is that 5 gram block of solid carbon dioxide is allowed to evaporate in a vessel of volume100 centimeter cube maintained at 20 degree centigrade. Calculate the work done when the system expands, part-a isothermally against a pressure of 1 atmosphere, and part-b isothermally and reversible to the same volume as in a. So, what you have is solid carbon dioxide and it is in a vessel of 100 centimeter cube.

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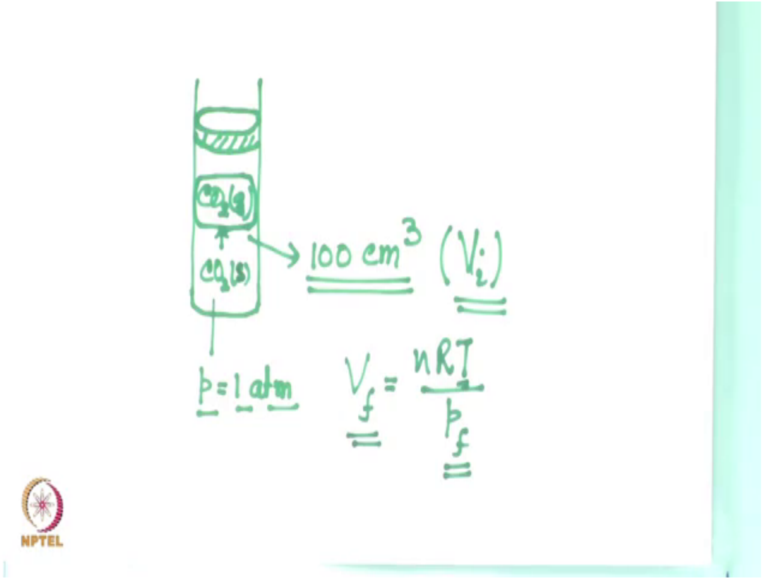

So, it is like you know you have a vessel, if I represent the vessel like this, and the total volume is 100 centimeter cube. And in this you have carbon dioxide solid and the pressure is equal to 1 atmosphere. Now, let us realize that based upon the phase diagram of carbon dioxide, carbon dioxide cannot exist in solid form at 1 atmosphere and 20 degree Celsius, it directly converts into vapors without going through liquid form. In order to have liquid carbon dioxide you need a pressure of minimum 5.11 bar. So, therefore, at 1 bar and 20 degree centigrade immediately carbon dioxide solid will convert to carbon dioxide gas.

So, essentially what you can treat that you have carbon dioxide with an initial volume of 100 centimeter cube. So, I can treat this as initial volume, now it is allowed to evaporate at 20 degree centigrade so that means, what will be the V f, V f again we will use ideality I will use this n R T over p f. The pressure is given 1 atmosphere, temperature is given 20 degree Celsius, and therefore, I can easily calculate V for final volume. So, once I have initial volume once I have final volume calculation is very, very easy.

Let us look at the slide V f is equal to n R T by p f, n is 5 divided by 44; 5 is the weight of carbon dioxide solid and 44 is its molecular weight, so 5 divided by 44 is the number of moles. R value here is being used in liter atmosphere per Kelvin per mole for obvious reason because we are using pressure in atmosphere. And use temperature in Kelvin 293.15 Kelvin, this gives a final volume of 2.734 liter. And since the expansion is against a constant pressure, we will use w is equal to minus p external into V f minus V i. And you substitute the values and the number that turns out to be is minus 2.634 liter atmosphere and then you multiply by 1 over 1.325 then convert into kilo Joules the answer is minus 0.267 kilo Joules.

And if the same thing were to be done under reversible conditions part-b, the formula to be used is minus n R T log V final over V initial and the substitution of the numbers various numbers give a value of minus 0.916 kilo Joules. And once again you see the work obtainable from the system is minus 916 Joules under reversible condition which is higher than the work obtained from the system that is 267 Joule when it is operating under irreversible conditions or when it is expanding under irreversible conditions against a constant external pressure.

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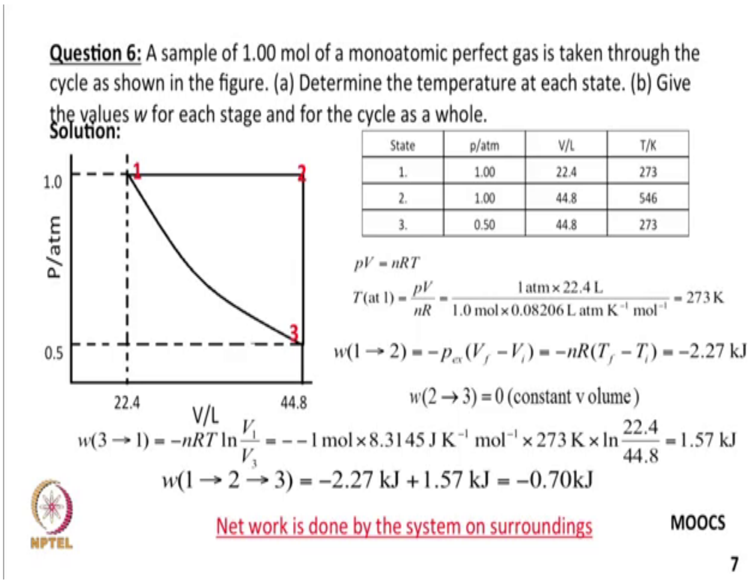

Question 6: A sample of 1.00 mol of a monoatomic perfect gas is taken through the cycle as shown in the figure. (a) Determine the temperature at each state. (b) Give the values *w* for each stage and for the cycle as a whole.

Solution:

State	p/atm	V/L	T/K
1.	1.00	22.4	273
2.	1.00	44.8	546
3.	0.50	44.8	273

$$pV = nRT$$

$$T(\text{at } 1) = \frac{pV}{nR} = \frac{1\,\text{atm} \times 22.4\,\text{L}}{1.0\,\text{mol} \times 0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}} = 273\,\text{K}$$

$$w(1 \rightarrow 2) = -p_{ex}(V_f - V_i) = -nR(T_f - T_i) = -2.27\,\text{kJ}$$

$$w(2 \rightarrow 3) = 0\,(\text{constant volume})$$

$$w(3 \rightarrow 1) = -nRT\ln\frac{V_1}{V_3} = --1\,\text{mol} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 273\,\text{K} \times \ln\frac{22.4}{44.8} = 1.57\,\text{kJ}$$

$$w(1 \rightarrow 2 \rightarrow 3) = -2.27\,\text{kJ} + 1.57\,\text{kJ} = -0.70\text{kJ}$$

Net work is done by the system on surroundings

MOOCS

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Last question in this tutorial is on a cyclic process. Let us consider a sample of 1 mole of a monatomic perfect gas which is taken through the cycle which I will show soon in the figure. Determine the temperature at each state give the values of work at each stage and for the cycle as a whole. This is the cycle you go from step one, stage one to stage two, and stage two to stage three, and then go back to stage one, this is the cycle. The first question is that determine the temperature at each stage.

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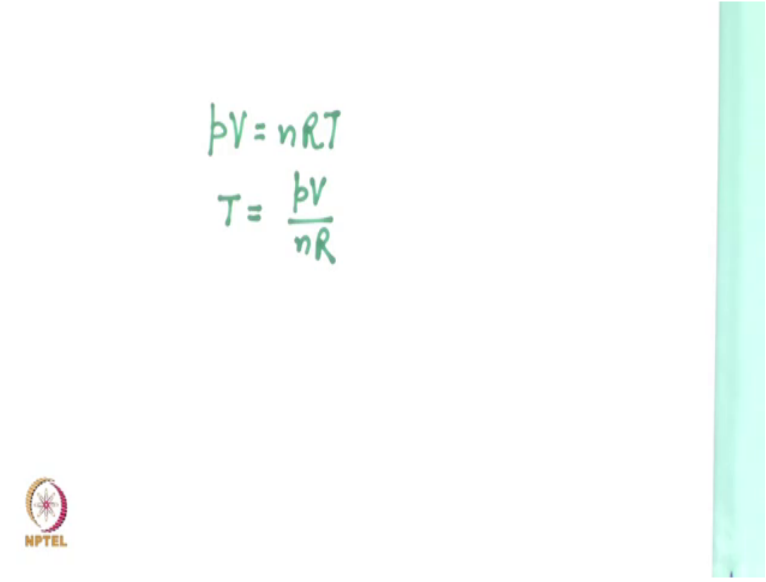

$$pV = nRT$$

$$T = \frac{pV}{nR}$$

And see it is a monoatomic perfect gas therefore, at each state p V is equal to n R T holds applies. Therefore, temperature can be easily calculated from p V is equal to n R whether the gas is at stage one or at stage two or at stage three as shown in the figure. So, once you use that formula T is equal to p V by n R at stage 1 where pressure is 1 atmosphere, volume is 22.4 liter, n is equal to 1, R using liter atmosphere per Kelvin per mole and you get a value of 273 Kelvin that is state 1. And 1 to 3, please note in the figure, 1 to 3 is an isothermal expansion, isothermal means temperature has to be same one can simply use this property isothermal; that means, the temperature at stage 1 and stage 3 has to be same that is 273 Kelvin.

However, at stage 2, where the volume is doubled; obviously, if the volume is doubled then using p V by n R, the pressure is same at stage 1 and 2, only the volume is doubled. So, therefore, the temperature according to the calculation should also be double the temperature then that at stage one that is 546 Kelvin.

Now, talk about process 1 to 2, 1 to 2 is a constant pressure process irreversible change. So, the formula to be used is minus p external into V f minus V i. Since, p V is equal to n R T has to hold you can also write this as minus n R into T f minus T i. Now, you can substitute any data, you can substitute the volume data or you can substitute the temperature data, you will get the same answer. So, w one to two turns out to be minus 2.27 kilo Joule. Now, let us see 2 to 3. Take a look at the figure, 2 to 3, and the volume is constant. So, if the volume is constant, there is no work done. So, straightaway the work is equal to 0, it is a constant volume.

3 to 1 that curve belongs to isothermal reversible compression. So, therefore, the formula to be used is minus n R T log V 1 by V 3, because V 1 is the final volume and V 3 is the initial volume. Now you substitute the numbers, please note here I am using R here in Joules per Kelvin per mole because I want the final answer in Joules and the answer comes to 1.57 kilo Joule. So, 1 to 2 minus 2.27 kilo Joules of work is done by the gas. 2 to 3 is a constant volume process it is 0; and 3 to 1, 1.57 kilo Joules of work is done on the gas. And if you add all over all the work is actually available, because the sign turns out to be negative and therefore, the work over all is done by the gas on the surroundings. So, w is minus 0.70 kilo Joules.

So, here also you see note that net work is done by the system on surroundings. Generally, in any cyclic process, if you talk about the state property if it were enthalpy if it were internal energy, if it were free energy, the overall change for a cyclic process would have been 0, but here when it comes to work it is nonzero. Once again this calculation these calculations establish that work is a path function; it is not a state property.

So, I hope that these numerical problems have let to understanding the basic concepts in a more clearer way, if still there are some queries some questions please do note down, those questions and we will definitely or resolve those queries and answer your questions in the help session.

Thank you very much.