

**Chemical Principles II**  
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**Module 03**  
**Lecture 21**  
**Tutorial Problem – 02**

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Application of isothermal and adiabatic work: TQ3

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Say  $f(x,y)$  is a function of  $x$  and  $y$ .  $df$  is an exact differential if  $\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)\right]_y$

Based on the above definition, which of the following would be exact differentials?

①  $\rightarrow df = 6x^5 dx + dy$

②  $\rightarrow df = \cos x dx - \sin y dy$


③  $\rightarrow df = x dx + \sin y dy$

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

$= M dx + N dy$

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

①  $M = 6x^5$   
 $N = 1$   
 $\left(\frac{\partial M}{\partial y}\right)_x = 0$      $\left(\frac{\partial N}{\partial x}\right)_y = 0$



Now also there are different types of problems, so we are also we will like to do some exact differential problems so say if  $XY$  is a function of  $X$  and  $Y$  and  $DF$  is an exact differential only if you know the formula, only if this condition satisfies based on the above definition which of the following would be exact differentials, so if you remember the formula for exact differential was that I can write  $F$  as  $\frac{\partial F}{\partial X}$  at constant  $Y$   $DX$  plus  $\frac{\partial F}{\partial Y}$  at constant  $X$   $DY$ , which we were calling as  $MDX$  plus  $NDY$  so since the first  $M$  is the first derivative of  $X$  the condition of exact differential is I have to now do with that is derivative with respect to  $Y$  because we have already done with respect to  $X$  when calculate the  $N$ , now we have to do with respect to  $Y$  at a constant value of  $X$  has to be equal to so  $N$  is a derivative with respect to  $Y$  already so you have to do now with respect to  $X$  is this condition is satisfies then it will be in exact differential, Now we have to identify what is  $M$  and what is  $N$ , as you can see  $M$  is six in the first problem,  $M$  is six  $X$  to the power 5 and  $N$  is one.

So let us calculate for the first problem let us say I call to one two and three let us say for first problem one M is six X to the power 5 and N equal to one, so del M by del Y as at the function of X is zero, there is no Y dependence and del N by del X are constant Y is also zero because we are just doing for this thing so first one is an exact differential, Now I to erase it.

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Application of isothermal and adiabatic work: TQ3


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Say  $f(x,y)$  is a function of  $x$  and  $y$ .  $df$  is an exact differential if  $\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)\right]_y$

Based on the above definition, which of the following would be exact differentials?

$\textcircled{1} \rightarrow df = 6x^5 dx + dy$   
 $\textcircled{2} \rightarrow df = \cos x dx - \sin y dy$   
 $\textcircled{3} \rightarrow df = x dx + \sin y dy$

$M = \cos x$   
 $N = -\sin y$   
 $\left(\frac{\partial M}{\partial y}\right)_x = 0$   
 $\left(\frac{\partial N}{\partial x}\right)_y = 0$



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Now let us do the second one, for the second one M is Cos X and N is minus Sin Y that you don't forget because we are always talking about classes now it is minus Sin Y so as I said M is already a derivative with respect to X that is why it is and how do you know that whether it is a derivative with respect to X or not because we can see there is a DX here which means this must be already a derivative of X, now we have to check with respect to Y so del M by del Y at a constant value of X is equal to zero del N by del X at a constant Y is also zero.

So did you understand this particular part that Y, I am identifying this Cos X as already a derivative with respect to X because I have to do DF by DX at a constant Y then DX so because there is a DX here which means this is already a derivative with respect to X, now I have a derivative with respect to Y, M and N does not matter what matters is that what was the first derivative so you see that this is also an exact differential.

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### Application of isothermal and adiabatic work: TQ3

Say  $f(x,y)$  is a function of  $x$  and  $y$ .  $df$  is an exact differential if  $\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)\right]_y$

Based on the above definition, which of the following would be exact differentials?

- ①  $\rightarrow df = 6x^5 dx + dy$
- ②  $\rightarrow df = \cos x dx - \sin y dy$
- ③  $\rightarrow df = x dx + \sin y dy$

$$df = \sin y dx + x dy$$
$$\left(\frac{\partial}{\partial y} \sin y\right)_x = \cos y$$
$$\left(\frac{\partial}{\partial x} x\right)_y = 1$$

*inexact differential.*



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Now comes a third one hopefully it will be not because otherwise will not learn what is this thing so again  $X$  is already derivative with respect to  $X$  so now I have to do with respect to  $Y$ , which is of course going to be zero and then right hand side I have to do with respect to  $X$ , and which is going to be zero, let us change that let us do different one, let us give you another DF which is  $M$  just changing instead of  $XDX$  and  $\sin YDY$  I am taking the three and reversing it,  $\sin Y DX$  plus  $XDY$  I have just reverse it so now I have to do with respect to in order to calculate that since already I have  $DX$  here which means first derivative was already with respect to  $X$  which is  $\sin Y$ .

Now I have to do with respect to  $Y$  so  $\frac{\partial}{\partial y} \frac{\partial}{\partial y} \sin Y$  at a constant value of  $X$  is equal to  $\cos Y$ , and  $\frac{\partial}{\partial x} \frac{\partial}{\partial x} X$  at a constant value of  $Y$  equal to one and now they are not equal,  $\cos Y$  is not equal to one and they are for this DF is not an exact differential, so this is an inexact differential, so if I interchange this another one that also will be the same thing.

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### Application of isothermal and adiabatic work: TQ3

Say  $f(x,y)$  is a function of  $x$  and  $y$ .  $df$  is an exact differential if  $\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)\right]_y$

Based on the above definition, which of the following would be exact differentials?

- ①  $\rightarrow df = 6x^5 dx + dy$
- ②  $\rightarrow df = \cos x dx - \sin y dy$
- ③  $\rightarrow df = x dx + \sin y dy$

$$df = -\sin y dx + \cos x dy$$
$$\frac{\partial}{\partial y}(-\sin y)_x = -\cos y$$
$$\frac{\partial}{\partial x}(\cos x)_y = -\sin x$$

*inexact differential*



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So for example if I take the second one and interchange this DF equal to minus Sin Y DX plus Cos X DY so I have to take derivative with respect to Y for the minus Sin Y, so del del Y of minus Sin Y is minus Cos Y at a constant X and del del at X of Cos X at a constant Y is minus Sin X and they are not equal therefore this is also not an exact differential it is an inexact differential.

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### Application of isothermal and adiabatic work: TQ4

Obtain a relation between  $(\partial H/\partial U)_P$  and  $(\partial U/\partial V)_P$ .

$$\begin{aligned} H &= U + PV \\ dH &= dU + PdV + VdP \\ \left(\frac{\partial H}{\partial U}\right)_P &= 1 + P\left(\frac{\partial V}{\partial U}\right)_P + 0 \\ &= 1 + \frac{P}{\left(\frac{\partial U}{\partial V}\right)_P} \quad \left(\frac{\partial V}{\partial U}\right)_P = \frac{1}{\left(\frac{\partial U}{\partial V}\right)_P} \end{aligned}$$



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So now comes another problem obtain a relation between  $\partial H$  by  $\partial U$  at a constant  $P$  and  $\partial U$  by  $\partial V$  at a constant  $P$ , we have to see that both are kind of at a constant pressure, and we also know the relation between  $H$  and  $U$  so  $H$  is  $U$  plus  $PV$  so  $dH$  will be what?  $dU$  plus  $PdV$  plus  $VdP$  every term will be there because we did not put any condition yet as of yet.

Now we are going to take that derivative with respect to  $U$   $\partial H$  by  $\partial U$  at a constant  $P$ , so it will be  $\partial U$  by  $\partial U$  going to be one, plus  $P$   $\partial V$  by  $\partial U$  at a constant  $P$  plus  $\partial V$  by  $\partial U$  at a constant  $P$  but  $dP$  is Zero so this term will be zero now you see becomes very simple is that  $\partial H$  by  $\partial U$  at  $P$ , I have got  $\partial U$  by  $\partial V$  we got  $\partial V$  by  $\partial U$  though but we can manage that so which means that I can write that one plus  $P$  by  $\partial U$  by  $\partial V$  at  $P$  it is in a reciprocal relation so what I am saying that  $\partial V$  by  $\partial U$  at  $P$  is one by  $\partial U$  by  $\partial V$  at  $P$ , we will see that we can write that is a reciprocal relation.

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### Application of isothermal and adiabatic work: TQ5

Write expressions for  $dV$  and  $dP$  given that  $V$  is a function of  $p$  and  $T$  and  $p$  is a function of  $V$  and  $T$ . (b) Deduce expressions for  $d(\ln V)$  and  $d(\ln P)$  in terms of the coefficient of thermal expansion  $\alpha$  and the isothermal compressibility  $k_T$ . [ $\alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_P$  and  $k_T = -\frac{1}{V} \left( \frac{dV}{dP} \right)_T$ ]

$$\begin{aligned}
 V &\equiv V(P, T) \\
 P &\equiv P(V, T)
 \end{aligned}
 \left. \begin{aligned}
 dV &= \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT \\
 dP &= \left( \frac{\partial P}{\partial V} \right)_T dV + \left( \frac{\partial P}{\partial T} \right)_V dT
 \end{aligned} \right\}$$

$$(b) \quad d \ln V = \frac{1}{V} dV = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T dP + \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P dT$$

$$d \ln V = -k_T dP + \alpha dT$$

$$d \ln P = \frac{1}{P} \left( \frac{\partial P}{\partial V} \right)_T dV + \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_V dT = \frac{1}{k_T P V} dV + \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_V dT$$

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So another one that write expression for DV ad DP given that V is a function of P and T so V is a function of P and T and P is a function of V and T, DV and DP given that so that is very simple right because V is a function of P and T means we can write DV as del V by del P TDP plus del V by del T PDT and similarly you can write P also the same way DP equal to del P by del V TDV plus del P by del T VDT you can write this too, now deduce the expression for DL and V.

So problem is done this is how do you express the DV and DP, basically how to write a total differential now problem BU is deduce expressions for DLNV so DLNV is what, what is DLNV, one by V DV that is the DLNV and we already know DV so you can just write DLNV just by dividing DV by one by V, so it will be this term divide by one by V and DLNP in terms of the coefficient of thermal expansion this is isothermal compressibility and this is coefficient of thermal expansion which tells you that given a temperature how much change of the volume will be there and unit change of the volume so you can see that this alpha equal to one by V alpha is the coefficient of thermal expansion.

So let us say if the temperature changes by one degree at a constant pressure how much the volume will change and normalize by the volume, so that give you an idea that what is how much expansion is possible for a liquid or gas or whatever more something will expand less

depending on the alpha and this is called isothermal compressibility, why isothermal so because the temperature is fixed and say how much is the gas can be compressed and that's why this is a negative sign, because negative sign indicates compression, how much the volume change will be there if you pressure the system, so this are the quantities also called heat capacities apart from CP and CV so and these are all measurable quantities you will see in future that for any kind of partial derivatives people should express in term of this quantities.

So that we can calculate them experimentally actually we can measure them experimentally rather, we can calculate the value using the experimentally measurable quantities which is this alpha and  $K_T$ , now you can see so one by  $\frac{dV}{dP}$  which means it is  $\frac{dV}{dP}$  so one by  $\frac{dV}{dP}$   $\frac{dV}{dT}$  so I am writing  $\frac{dV}{dT}$  plus one by  $\frac{dV}{dT}$   $\frac{dV}{dT}$   $\frac{dV}{dT}$ , now what is one by  $\frac{dV}{dT}$   $\frac{dV}{dT}$   $\frac{dV}{dT}$  at a T is minus  $K_T$ , so it is minus  $K_T$   $\frac{dV}{dT}$  and what is one by  $\frac{dV}{dT}$   $\frac{dV}{dT}$  this is alpha T so alpha  $\frac{dV}{dT}$ , so we are express  $\frac{dV}{dT}$  in terms of this measurable quantities  $K_T$  and alpha so given this  $K_T$  and alpha if there is a change in temperature we will know how much change in  $\frac{dV}{dT}$  will be there, similarly  $\frac{dV}{dT}$  also one can write as  $\frac{dV}{dT}$  as one by  $\frac{dV}{dT}$   $\frac{dV}{dT}$  plus one by  $\frac{dV}{dT}$   $\frac{dV}{dT}$ .

Now here you can see that it is instead of  $\frac{dV}{dT}$  it is  $\frac{dP}{dT}$  just the opposite of that so  $\frac{dP}{dT}$  will be from this equation minus one by  $K_T$ , minus one by  $K_T$  into  $\frac{dP}{dT}$  plus what is  $\frac{dP}{dT}$ , so  $\frac{dP}{dT}$  is not there we cannot write that directly as this isothermal compressibility's so we have to wait for this quantity to be expressed in terms of compressibility's when we will discuss about how to change this partial derivatives into different forms that time we will discuss about what will be the measure corresponding values of this one, but of them will be possible to be converted in term of this measurable quantities such as specific heats, CPCV, alpha and  $K_T$  and there are some adiabatic compressibility which is called there are  $(\gamma)$ (13:22).

So the point is that whatever partial derivative will give it should be able to get a value of those by or express in terms of measurable quantities, experimentally measurable quantities and experimentally everything you cannot measure, you cannot measure the change in you, you can measure probably enthalpy, you can measure heat, you can measure pressure, you can measure volume, you can measure change in volume with respect to pressure, you can measure change in

volume with respect to temperature but you cannot measure change in enthalpy when you change in internal energy, you cannot measure that at a given entropy for that we need to convert it to something that we can measure and that is a whole thing that we learn later on.

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#### Application of isothermal and adiabatic work: TQ6

Show that,  $\left(\frac{dU}{dT}\right)_p = \left(\frac{dU}{dT}\right)_V$  for ideal gas.

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

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

$$= \left(\frac{\partial U}{\partial T}\right)_V$$



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And this is very simple show that DU by DTP called to DU DTV for idea gas so remember we will do that again DV called to del U del VTDV plus del U by del TVDT, now we have to do one more derivative which is del U by del TP which is del U by del VT del V by del TP plus del U by del TV, del T by del T just one, now you already know that del U del VT is zero so this quantity become zero and it gives us del U by del TV, so for ideal gas in a change in internal with respect to temperature does not matter whether it do with at a constant pressure or a constant volume, does not matter in fact when it is at constant volume and temperature does not change means pressure also does not change so we will stop here.