

hello students welcome to lecture  
four of chemical equilibrium i will start with recap which i did  
in the last lecture that is your in the last lecture i discussed  
about leachate earlier principle the most important use of le chatelier's  
principle is we can know under what condition a reaction can give maximum  
product a reaction  
can give maximum yield what do i mean by condition we can change concentration  
we can change pressure  
we can change volume and we can change temperature  
so if we understand leachate earlier principle you  
will be able to tell if i increase the temperature whether reaction will go to  
right hand side means  
more product will form or less product will be formed similarly if i increase  
the pressure  
and what will happen to the reaction whether reaction will shift towards  
forward direction  
or reaction will shift towards reverse direction what leachate earlier principle  
tells you it tells  
you that if we alter the conditions for example pressure temperature of volume  
we can disturb  
the equilibrium we can disturb the equilibrium finally a new equilibrium will  
be established this  
principle tells you that new equilibrium will be in which direction whether  
equilibrium will  
shift to right hand side or left hand side the law tells you that equilibrium  
will shift to  
that direction which tends to minimize the change equilibrium will shift to  
that direction  
which tends to minimize the change then we looked at the effect of increase in  
pressure  
so suppose i am increasing the pressure that can be done by decreasing the  
volume ok i showed you that in that case  $\Delta n$   
if  $\Delta n$  is positive reaction will move towards reverse direction or  
reverse  
reaction will be favored what i mean by  $\Delta n$  is your change in strike you  
matri  
so basically it is  
the stoichiometry of product minus stoichiometry of reactant if this is  
positive then reverse  
reaction will be favored if it is negative then forward reaction will be  
favored when we  
increase the pressure  
so this is about when i increase the pressure  
so if reaction has  $\Delta n$   
is positive increase in pressure will favor the reverse reaction whereas if  
 $\Delta n$  is negative  
increase in pressure will favor forward reaction pressure can be changed in  
another way  
pressure can be changed can be changed by introducing introducing your inert gas  
inert gas  
so first condition we discuss that when we  
change pressure by decreasing the volume or increasing the volume pressure  
will be  
increased if we decrease the volume whereas pressure will decrease when we

increase

the volume but we can increase the volume we can increase the pressure by introducing

inert gas keeping volume constant so suppose i am taking a closed container closed

container and then we have molecules of a and b is your reactant b is product i can

increase the pressure by introducing another gas which does not interact with a or b which

does not interact with a and b and that is basically you are introducing inert gas overall pressure is increased volume has

not increased ok in that case what happens

so i discuss this reaction  $p_{c1} \rightleftharpoons p_{c2}$  gas

giving you  $p_{c1} \rightleftharpoons p_{c2}$  gas plus  $cl_2$  gas  $cl_2$  gas in this case  $k_p$  can be

written as pressure of  $p_{c1}^3$  into pressure of  $p_{c2}$  divided

by pressure of  $p_{c1}^5$  and pressure is your mole fraction of  $p_{c1}^3$

multiplied by total pressure into mole fraction of  $p_{c2}$  multiplied by total pressure divided by

mole fraction of  $p_{c1}^5$  into total pressure and then this can be written and mole fraction

can be written as  $n_{p_{c1}^3}$  divided by  $n_t$  where  $n_t$  is total amount of gas total number of

gaseous molecule this not only includes reactant and product but also includes inert gas

so  $n_t$

multiplied by  $n_{p_{c2}}$  divided by  $n_t$  into  $k_p$  this is also into  $k_p$  ok divided by again  $n_{p_{c1}^5}$

five by  $n_t$  into  $p_{c1}^3$   $p_{c1}^5$  cancels out one  $n_t$  one  $n_t$  cancels out

so what we are

left with  $n_{p_{c1}^3}$  into  $n_{p_{c2}}$  divided by  $n_{p_{c1}^5}$  ok and then one pressure left

this side pressure by  $n_t$

so now you see you have this quantity and  $k_p$  your the direction will depend on

whether  $p$  by  $n_t$  is increasing or decreasing if it increases then what will happen this

value will decrease to keep  $k_p$  constant while if this decreases this will increase

to keep  $k_p$  constant

so what happens you see  $p$  by  $n_t$  i told you that reaction

was carried out in closed container what does that mean is you have a constant volume

condition under constant volume and temperature

so  $p$  by  $n_t$  is constant  $p$  by  $n_t$  is constant

and

so basically this does not changes and so there is no need for change in this quantity

what does that mean is that introduction of inert gas will not have an effect on a reaction

if reaction is if pressure is increased by addition of inert gas at constant volume

so in a closed container in a closed container container which means constant volume system introduction of introduction

of inert gas inert gas does not have effect on the reaction even if there is



to temperature effect of temperature effect of temperature on equilibrium effect of temperature on equilibrium

so effect of temperature will depend on whether reaction is effect of temperature will

depend on whether reaction is reaction is exothermic exothermic or endothermic endothermic if reaction is your exothermic if reaction is is exothermic exothermic

so basically  $\Delta H$  is your negative what does this mean exothermic means a plus b giving you c plus d and heat is released plus heat released in this case if i increase the temperature if we increase the temperature increase the temperature temperature reaction will shift towards that side the reaction will shift will shift to the direction where heat is absorbed where heat is absorbed absorb since in exothermic heat is released so

heat is absorbed for a reverse reaction

so if i increase the temperature if i increase the temperature the reaction well shifts towards your reverse direction the reaction

will shift towards reverse direction

so basically exothermic reaction

exothermic reactions exothermic reactions are favored at low temperature if i go to if i take reaction which endothermic ok endothermic endothermic it means your heat is absorbed it is absorbed  $\Delta H$  is your greater than zero

so it is positive in this case if i increase the temperature

if we increase the temperature the temperature if we increase the

temperature forward reaction will be fewer favor since in the forward

reaction heat is absorbed in the forward reaction heat is absorbed favored now

lets understand what happens to  $K_p$  to  $K_p$  with temperature with temperature

before that we told that  $K_p$  does not

change with number of moles of pressure pressure or volume but  $K_p$  depends on temperature

$K_p$  depends on temperature  $K_p$  depends on temperature the equation which governs

the effect of the effect of your temperature the equation which govern effect

of temperature on  $K_p$  or  $K_c$  is given by  $\frac{d \log K_p}{dt}$  at constant pressure is equal to

$\frac{\Delta S^\ddagger}{R T^2}$  ok

so  $K_p$  will depend on the temperature dependence of  $K_p$  will

depend on  $\Delta H^\ddagger$

so if i take endothermic reaction endothermic reaction reaction your  $K_p$  increases with increase in

temperature increase in temperature while  $K_p$  for exothermic

reaction exothermic reaction  $K_p$  decreases with increase in temperature  $K_p$

decreases means your product well will decrease and reactant will increase

increase and that means is that reverse reaction reaction is favored reverse

reaction is failure

so in summary your exothermic reaction exothermic reactions are favored at low

temperatures low temperature whereas endothermic

endothermic reactions are reactions are favored at favored at high temperature

now lets take some example and see what happens when we increase the

temperature

so effect of temperature

so first reaction is your  $SO_2$  gas plus

$O_2$  gas giving you  $SO_3$  gas

so when  $SO_2$  reacts with  $O_2$  to give  $SO_3$

o three your heat is released it is released and it is an exothermic reaction and  $\Delta H$

is equal to minus eighty kilo joule  $\Delta H$  is equal to minus one eighty kilo joule per mole since this is a exothermic reaction

if i want to increase the product what should we do we should go to low temperature

it should decrease the temperature because exothermic reactions are favored by

exothermic reactions are favored by your are favored at low temperature low temperature

so if we want higher yield of  $SO_3$  higher yield of

$SO_3$  we should decrease the temperature now let us take dissociation of  $N_2O_4$  the

second reaction is dissociation of dissociation of  $N_2O_4$

so  $N_2O_4$  gas dissociating to  $2NO_2$  gas  $2NO_2$  gas ok  $N_2O_4$

dissociating to  $NO_2$  gas in this case your reaction is basically endothermic it means that heat is absorbed during the process heat is

absorbed during the process  $\Delta H$  is positive

so if we want more dissociation if we want more dissociation we have to increase the temperature we have to increase the temperature

because endothermic reactions are endothermic reactions are endothermic reactions are your favored at endothermic reactions are

favored at high temperature can think of about several different cases

for example methanol production  $CO$  gas plus  $2H_2$  gas giving you  $CH_3OH$  gas and  $\Delta H$  is equal to  $\Delta H$

is equal to minus 270 kilo joule per mole now again you see this to know the effect of to know the effect of

temperature on a reaction we must know whether it is the reaction is happening with

release of heat or absorption of it in this case heat is released and

so this reaction will be favored at low temperature low temperature means if we decrease the temperature we are we can expect to get higher amount

of methanol higher amount of methanol now we can use it in oppositions also

so suppose

a reaction  $A + B \rightarrow C + D$  lets take this in gases form ok if we know that with

increase in temperature increase in temperature product is increasing product is increasing that will give you clue

about whether heat is absorbed or released in a reaction since product is favored when

i increase the temperature it means that heat must have been absorbed in the system  $\Delta H$

absorbed during the reaction what does that mean is that your reaction is endothermic

reaction

so reaction is endothermic reaction is endothermic on the other hand i get with increase

in temperature increase in temperature the amount of product decreased

decreased then we can simply say that your reaction

is exothermic reaction is exothermic reaction is exothermic

so just by

looking at reactant and product how much they increased when we increase the

temperature we can tell whether a reaction is endothermic or exothermic heat is absorbed or released

so we just saw the effect of concentration pressure inert gas and temperature

on the equilibria now we know what will happen if i increase the temperature if i increase

the pressure if i introduce the inert gas and we can know in which direction reaction will shift and that can be applied if i want to increase the product if we want to increase the product

so this information will help you whenever you are trying to carry out a synthesis

so let us go and see some more examples some more examples for example let us take this case  $S_2 + 2H_2 \rightleftharpoons 2H_2S$  plus

$2H_2$  gas giving you  $2H_2S$  i guess which i guess now suppose i want to know the effect of your pressure effect of pressure effect of pressure effect of pressure

so must remember that last time i did showed you what will happen when we alter the condition

so see this just want to show you that we discussed what will be the effect of increase in pressure if  $\Delta n$

$\Delta n$  is positive reverse reaction will be favored with increase in pressure whereas if  $\Delta n$  is

negative then forward reaction will be favored with increase in pressure now lets see

what is  $\Delta n$  here so  $\Delta n$  is your you see this case two moles of  $H_2S$  so two this is the product minus reactant reactant is what one plus one

so this is zero this is zero so what does that mean is pressure will not affect pressure will not affect the reaction if suppose we increase the volume to double

pressure will decrease but since  $\Delta n$  is zero so even the effect there will no no no effect of increasing or decreasing the volume no effect of inert gas either even at constant pressure since  $\Delta n$  is zero

only thing which can affect this reaction is temperature

so if it is an endothermic reaction the effect of temperature will be different and if it is exothermic effect of temperature

will be different now lets take another example four  $N_2$  gas plus five  $O_2$  gas giving you

four  $N_2$  gas plus six  $H_2O$  gas six is two gas

so lets see whether it is balanced

or not four nitrogen four nitrogen twelve hydrogen 12 hydrogen 10 oxygen 4 oxygen plus 6 oxygen

or 10 oxygen

so this is your balance equation and we want to see the effect of pressure volume

anode gas or temperature

so let us see  $\Delta n$  first we have to calculate  $\Delta n$   $\Delta n$  is your stoichiometry of product

so four plus six ten minus four plus five nine is equal to

one

so it is positive it is greater than zero it means there will be effect of pressure

there will be effect of pressure here  $\Delta n$  is your  $\Delta n$  is positive and that means that if

i increase the pressure if i increase the pressure reverse reaction will be favored reverse reaction will be favored if i

increase the volume pressure will decrease pressure will decrease and your forward reaction will be favored

so if i increase the pressure reverse reaction

will be favored if i increase the volume your forward reaction will be favored effect

of inert gas if i keep volume constant if you are doing that in a closed container then there will be no effect but if we take the case of constant pressure

i introduced inert gas such that pressure is constant in that case your forward reaction

will be favored forward reaction will be now suppose take  $S_2 + C_2H_2$  gas this is your  $S_2 + C_2H_2$

two kilo joule ninety two kilo joule if suppose this is given ok now lets think of

what is effect of pressure temperature and volume what is effect of pressure temperature on board

now you see this that your 92 kilo joule of heat is released

so this is your exothermic reaction

this is your exothermic reaction in that case temperature will have effect whatever pressure and volume for pressure

so looking for ah looking at

effect of pressure of volume at equilibrium we must calculate  $\Delta n$  and  $\Delta n$  is

your two minus one plus one which is zero what does that mean is increase or decrease

in pressure will not affect this reaction not affect this reaction all are in gaseous phase

all are in gases phase ok but introduction of again introduction of inert gas will also not

affect this reaction whether it is carried out at constant volume or constant pressure only

thing which is going to affect this reaction is your temperature and since this is a exothermic

reaction since this is a exothermic reaction your temperature increase in temperature will not

favor the reaction basically a low temperature will favor the reaction low temperature will

favor the reaction now take another case  $S_2$  gas plus  $I_2$  gas giving you  $2HI$

$HI$  gas and  $\Delta H$  is equal to twenty five kilo joule this is plus kilo joule what does

that mean is the reaction is your endothermic reaction is endothermic

so suppose if we

are trying to look at effect of pressure pressure or volume first we calculated  $\Delta n$  and  $\Delta n$  here is two minus one of  $S_2$  and one of  $I_2$  and

so this is

zero

so no effect of pressure volume no effect of pressure or volume what about others no effect of inert gas inert gas whatever temperature temperature will affect

because this is an endothermic reaction and endothermic reaction are favored at high temperature

so high temperature high temperature will increase the product which is  $H_2$  in this

case which is  $H_2$  in this case another reaction  $2NO_2 \rightleftharpoons N_2O_4$  giving you  $n_2 = 2$   $n_4 = 1$

and this is your  $\Delta H$  is negative what does that mean this is exothermic reaction

now we can see that this is also in gaseous form what is  $\Delta n$   $\Delta n$  is one

minus two which is minus one it means pressure volume will affect if  $P$  increase

the pressure first thing increase the pressure what will happen if  $P$  increase the

pressure of you see this is the minus one ok

so forward reaction will be favored favor if  $P$  increase the volume reverse reaction will be

further reverse reaction will be if  $P$  increase the temperature now you see this is exothermic reaction

and in exothermic reaction you do not exothermic reactions are not favored at high

temperature they are favored at low temperature so reverse reaction in this case

will happen will be favored another way to remember is that

increasing the temperature will shift the reaction toward that side in which heat is

absorbed

so if  $P$  take the reverse reaction in this case your  $\Delta H$  will be positive or heat will

be absorbed

so dissociation of  $N_2O_4$  is an endothermic reaction and

so with increase

in temperature reverse reaction this is this dissociation will be favored ok inert gas effect

of inert gas at constant volume it will not affect but at constant pressure your reaction will be reaction can be affected reaction can be affected it

will just opposite to this in this

case your reverse reaction will be favored now last is the effect of your

catalyst effect of effect of catalyst what

will happen

so effect of catalyst catalyst on the equilibrium equilibrium ok

so what happens

when  $P$  you add the catalyst know this is the potential energy

or energy versus reaction coordinate ok this is kind of safe we get this is your reactant this is your product and this is transition state this is the

transitions

so if we have a reaction and if we do add catalyst what can happen we know that

if  $P$  add a catalyst

so in presence of catalyst this curve will be something like this what does that mean reactant and this is product

and this is transition state

so catalyst basically stabilizes the transition state

so it went down from this point to this

so reaction activation energy decreased activation energy decrease

so reaction will be faster but does it affect equilibria ok question

is does it affect equilibrium catalyst does not affect equilibrium as an effective equilibrium because you see what is your  $k_f$  by  $k_b$   $k_f$  is your rate constant for forward direction

and  $k_b$  is rate constant for backward direction  $k_f/k_b$  changes when we add a catalyst but

the ratio does not change ok

so  $k_f$  changes  $k_b$  changes because activation energy will be lowered and if activation energy

for forward reaction is lowered it means  $k_f$  will increase but catalyst also decreases

activation energy of reverse reaction of the reverse reaction and so  $k_b$  also increases

so  $k_f$  changes there is increase in  $k_b$  increase in  $k_b$  and increase in  $k_f$  but the ratio remains constant  $k_f/k_b$  remains constant and that means that

there is no effect of catalyst on the equilibrium you can understand this from here

so what happens that you have energy versus reaction coordinates or extent of reaction you have this kind of curve and there is no

catalyst and this is activation energy for forward reaction this is activation

energy of reverse reaction reverse reaction or backward reaction when

i add a catalyst what i get is basically

so it is initially suppose this way it goes down the presence of catalyst

so initially

you have this is  $E_a$  activation energy of forward but in presence of catalyst it decrease to this

so this is  $E_a$  but you see activation energy of

reverse reaction also decreased activation energy of reverse reaction also decreased

so it was here first

so this is suppose  $E_a$  for a reverse reaction and now in presence

of catalyst this is decreased to this value and when this decrease to this value you

have a new  $E_a$  which is called  $E_a$  ok

so your equilibrium constant is this is  $k_f/k_b$   $k$  gets affected in presence of catalyst and it becomes  $k_f$  and  $k_b$  also changes

and that becomes  $k_b$  but the value of  $k_f/k_b$  and  $k_f$  by  $k_b$  will remain same

so catalyst increases the rate of reaction it increases rate of both reaction forward

and reverse direction or reverse reaction but the ratio of  $k_f$  and  $k_b$  does not change

so ratio of  $k_f$  and  $k_b$  does not change and

so catalyst catalyst does not affect the equilibrium does not affect the equilibrium

so in a nutshell we can change the direction of we can control a reaction by

changing changing conditions by changing conditions we can maximize the product  
maximize the product if maximize the product if we have understanding of  
understanding of lee chatelier's principle and that is why le chatelier's  
principle is very important when we are dealing with a chemical  
reaction thank you very much you

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