SHEET 1

FIRING PHENOMENA

1. The table refer to the bulk density (g.cm⁻³) of a mullite specimen fired at 1350°C.

Time min	0	10	20	30	40	50	60
ρ_B g.cm ⁻³	2.581	2.614	2.621	2.628	2.63	2.638	2.641

Predict the probable mechanism of initial sintering, then compare the rate of sintering after 10 min. and after 60 min.

- 2. It is known that sintering of KCl particles takes place in the early stages by an evaporation condensation mechanism. The initial bulk density is 1.42 g.cm^{-3} If the bulk density after 50 minutes sintering = 1.70 g.cm^{-3} , estimate the time required to reach a bulk density of 1.90 g.cm^{-3} .
- 3. A zircon alumina cylindrical specimen of height 80mm was prepared by pressing 105μ m particles. It was then fired to 1350° C for 30 minutes. The fired height = 79.2mm. If it is known that the early stages of sintering of that material take place be surface diffusion, estimate the final height of a similar cylinder consisting of 75 μ m particles sintered for 20 minutes at the same temperature.
- 4. Sintering of magnesia powder at 1400°C has produced the following data for the variation of bulk density with time. Find the time after which the initial stage ends.

Time min	0	5	10	15	20	25	40
ρ_B g.cm ⁻³	3.125	3.217	3.352	3.445	3.502	3.51	3.522

5. The following table shows the variation of the average grain size of barium titanate with time on sintering at 1280°C. Estimate the mean initial grain size.

Time h	10	15	20	25	30	35	40
D µm	47.0	53.5	57.1	60.8	64.9	73.3	77.8

6. Magnesium aluminate spinel (MgO.Al₂O₃) was pressed into cylindrical pellets at 120MPa. The following data were obtained for the percentage linear shrinkage at four different temperatures. Deduce the sintering mechanism and determine the activation energy for the initial sintering stage.

Time h	0	1	2	3	4	5
900	10.25	12.8	18	23	25.5	28.7
1000	10.25	13.3	19	23	26.4	29.8
1100	10.25	13.9	19.6	24	27.7	30.8
1200	10.25	14.45	20	25	28.8	32

SHEET 2

EQUILIBRIUM RELATIONSHIPS

- 1. At what equilibrium temperature will titanium oxidize in pure O_2 ? What pressure should be maintained to suppress oxidation up to 1600°C?
- 2. Can magnesium metal be safely oxidized in an alumina crucible? Why? And what about oxidizing titanium metal?
- 3. Over what temperature range will the following reaction take place? $2Cu + 3Fe_2O_3 = Cu_2O + 2Fe_3O_4$
- 4. NaCl melts at 801°C. The solid and liquid salts have respective densities of 2.172 and 2.156 g.cm⁻³. If an increase in pressure from 1 to 400 atm causes the melting point to increase to 801.32°C, what is the enthalpy of melting of the salt?
- 5. The enthalpy of vaporization of AgCl (kJ.mol⁻¹) is related to temperature (K) by the expression: $\Delta H_{\nu} = 184.2 0.0018T$. If its normal boiling point = 1550°C, what would be its boiling point under a pressure of 10 atm?
- The following figure represents the phase diagram ZrO₂ SiO₂ (On weight basis). Determine the intermediate compounds formed and their high temperature behavior. And the invariant situations occurring, stating the corresponding reactions and temperatures.



7. The following diagram illustrates equilibrium relations in the system $ZrO_2 - TiO_2$ on molar basis.

Determine the following:

- (a) The intermediate compounds formed and their high temperature behavior.
- (b) The invariant situations occurring, stating the corresponding reactions and temperatures and the composition of any liquid formed.



- 8. The following figure illustrates the phase diagram $FeO TiO_2$ on molar basis. Answer the following questions:
 - (a) On this diagram, mark the phases present.
 - (b) Enumerate the intermediate compounds formed and describe their melting behavior.
 - (c) Write the invariant reactions occurring, mentioning their type, temperature and percent liquid formed (If any).

(d) At a temperature = 1385° C, is drawn an isothermal line; roughly plot the percentage liquid against mol fraction of TiO₂.



9. The figure shows the diagram V_2O_5 – CaO (on weight basis). Identify the invariant reactions, mentioning their type, temperature and percent liquid formed. Then, determine the temperature at which a composition containing 30% CaO must be heated to obtain a percent liquid = 70%.



SHEET 3

KINETICS OF SOLID STATE REACTIONS

- 1. The oxidation of graphite spherical particles is known to take place by a shrinking sphere mechanism R3. When 34.5g of graphite were subjected to oxidation in air at 900°C, the original mass dropped to 26.7g after 5 minutes. Determine the time required for complete oxidation if the ash residue = 0.87g.
- 2. Spherical particles of zinc sulfide of particle radius = 1mm are roasted in oxygen at 900°C and 1 atm. The following reaction takes place following a chemical reaction mechanism: $ZnS + O_2 = ZnO + SO_2$. The nucleation of ZnO was found to be controlled by a progressive reaction model (Avrami Erofeev), with n = 2.

If 50% of the reaction takes place in 17 minutes, evaluate the time required to complete 99% of the reaction.

- 3. The decomposition of cobalt oxalate at 250°C has been properly interpreted by the progressive reaction model. The fractional conversion = 0.38 after 24 min and 0.65 after 72 min. Evaluate the value of the constant *n* in the Avrami Erofeev equation.
- 4. Cylindrical tungsten carbide (WC) pellets were formed by hot pressing and subjected to an air stream at 1150°C to investigate the oxidation mechanism according to:
 2 WC (s) + 5 O₂ (g) = 2 WO₃ (s) + 2 CO₂ (g) (W = 184, C = 12, O = 16). If the original mas of the pellet = 8.75 g, what is the mass after full oxidation? It was found that the reaction was controlled by a two-dimensional diffusion mechanism D2. If full oxidation is completed in 74 minutes, evaluate the time it would take for the mass to reach 9.8 g.
- 5. From the following data illustrating the mass variation with time of the reaction of barium carbonate with silica to produce barium silicate. Prove that this reaction is controlled by diffusion through unreacted ash (D3). What is the time required to complete the reaction?

Time min	1	4	9	17	30	48	75
Conversion	0.1	0.2	0.3	0.4	0.5	0.6	0.7

6. The following data refer to the percent recovery of aluminum from casting waste by fusion with caustic soda at 700°C. prove that these data conform to a 1st order reaction model.

Time min	5	10	15	40	60	70
Conversion %	22	29	51	78	90	94

- 7. Prove that in a solid-state shrinking sphere controlled reaction R3, the time required for full conversion is about 5 times that for 50% conversion.
- 8. The following data relates to the dependence of the rate of conversion (min⁻¹) on conversion during the oxidation of lead sulfide at 300°C. Prove that this reaction is controlled by R3 reaction mechanism and determine the reaction rate constant at that temperature.

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$d\alpha/dt$	3	2.8	2.56	2.25	2	1.77	1.42	1.1	0.71

9. The following figure illustrates the TG – DTG curve obtained for the pyrolysis of wheat straw at a heating rate of 10°C.min⁻¹ in a flow of nitrogen. Consider the first decomposition step to start at 260°C and to end at 340°C. If a first order model F1 is assumed for that step, use the Coats – Redfern method to evaluate the activation energy of the first decomposition step.



10. The following DTG curves were obtained for the decomposition of nitrocellulose in inert atmosphere. Use the Kissinger method to evaluate the activation energy.



11. The following data relate to the pyrolysis of a vegetable waste in nitrogen atmosphere at different heating rates. Temperatures are expressed in °C. Use the FWO method to determine the value of activation energy over the given composition range.

β°C.min ⁻¹	5	10	15	20
$\alpha = 0.2$	254.9	263.9	270.6	275.2
0.3	271.4	280.3	287.1	292.5
0.4	285.2	294.1	301.4	307.4
0.5	297.1	306.0	313.8	320.2
0.6	308.0	317.1	324.9	331.8
0.7	319.3	328.4	336.1	343.8
0.8	333.3	342.6	349.4	359.7

12. Repeat the previous problem using the KAS technique

CHE610: SOLUTIONS TO SHEETS

SHEET 1: Firing Phenomena

t min	0	10	20	30	40	50	60
ρ_B g.cm ⁻³	2.581	2.614	2.621	2.628	2.63	2.638	2.641
$\Delta L/L_0$	0	0.00422	0.00511	0.006	0.00625	0.00725	0.0076
ln t		2.30258	2.99573	3.4012	3.68888	3.91202	4.0943
$\ln \Delta L/L_0$		-5.46661	-5.276	-5.1165	-5.0754	-4.9262	-4.876

1. The following table is set:

A plot of $\ln \frac{\Delta L}{L_0}$ against ln *t* yields a straight line of **slope = 0.33** (R² = 0.983). Hence, this is a **grain boundary-controlled diffusion**.

2.
$$\rho_0 = 1.42, t = 50 \rightarrow \rho = 1.7 \rightarrow \frac{\Delta L}{L_0} = 1 - \left(\frac{\rho_0}{\rho}\right)^{\frac{1}{3}} = 0.05817$$

 $\frac{\Delta L}{L_0} = k.t^{2/3} \rightarrow 0.05817 = k \times 50^{2/3} \rightarrow k = 0.00429$
 $\rho = 1.9 \rightarrow \frac{\Delta L}{L_0} = 1 - \left(\frac{1.42}{1.9}\right)^{\frac{1}{3}} = 0.09249 = 0.00429t^{\frac{2}{3}} \rightarrow t = 100.1 \text{ min}$

3
$$\Delta L = 80 - 79.2 = 0.8 \text{ mm} \rightarrow \frac{\Delta L}{L_0} = 0.01 = k \frac{t^{0.4}}{D^{0.6}} = k \times \frac{30^{0.4}}{105^{0.6}} \rightarrow k = 0.04187$$

 $\frac{\Delta L}{L_0} = 0.04187 \times \frac{20^{0.4}}{75^{0.6}} \rightarrow \frac{\Delta L}{80} = 0.010406 \rightarrow \Delta L = 0.8325 \rightarrow L = 79.1675 \text{ mm}$

4. The following table is set:

t min	0	5	10	15	20	25	40
ρ_B g.cm ⁻³	3.125	3.217	3.352	3.445	3.502	3.51	3.522
$\Delta L/L_0$	0	0.00962	0.0231	0.03197	0.03725	0.03798	0.03908
ln t		1.6094	2.3026	2.7080	2.9957	3.2188	3.6889
$\ln \Delta L/L_0$		-4.64339	-3.76779	-3.44283	-3.28998	-3.2705	-3.2421

The linear portion ends at about t = 20 min



5.

Time h	10	15	20	25	30	35	40
D µm	47.0	53.5	57.1	60.8	64.9	73.3	77.8
D^2	2209	2862.25	3260.41	3696.64	4212.01	5372.89	6052.84

The relation between D^2 and t is linear with $R^2 = 0.9711$. its equation is:

 $D^2 = 826.51 + 125.03t \rightarrow D_0^2 = 826.51 \rightarrow D_0 = 28.75 \mu m$

6.

$\Delta L/L_0$	0	1	2	3	4	5
900	0.1025	0.128	0.18	0.23	0.255	0.287
1000	0.1025	0.133	0.19	0.23	0.264	0.298
1100	0.1025	0.139	0.196	0.24	0.277	0.308
1200	0.1025	0.1445	0.2	0.25	0.288	0.32

Plots of $\ln \frac{\Delta L}{L_0}$ against $\ln t$ at the four temperatures yield the following slopes and intercepts for the expression: $\frac{\Delta L}{L_0} = Ct^{0.5}$

Т°С	90	1000	1100	1200
Slope n	0.504198	0.49702	0.49558	0.4986
$1/T { m K}^{-1}$	0.000853	0.00079	0.00073	0.00068
Intercept ln C	-2.05376	-2.014	-1.9728	-1.9403

Hence, sintering is controlled by **bulk diffusion**.

The plot of ln *C* against 1/T yields a straight line (R² = 0.9985) of slope = -658.13, corresponding to an activation energy = **5471.7 J.mol**⁻¹

SHEET 2: Equilibrium Relationships

- 1. At $p_{O_2} = 1$ atm, the base line intercepts the TiO₂ oxidation line at about **1300°C** To suppress oxidation at 1600°C. join the base line to the point on the TiO₂ oxidation line at that temperature. You get on the p_{O_2} axis, about $p_{O_2} = 0.01$ atm
- The line of Mg oxidation being lower than that of Al oxidation, MgO will be a stable phase so that it expected that the following reaction will have a negative free energy value: Mg + Al₂O₃ = Al + MgO, meaning that the crucible material will deteriorate.

In case of oxidizing Ti in an alumina crucible, the line of oxidation of Al is lower than that of Ti and so, Al₂O₃ will remain as stable phase and no deterioration of the crucible material will take place.

3. For that reaction to take place, it is necessary that Fe₃O₄ remains a stable phase. This is secured above about 680°C, where the oxidation of Cu will take place rather than that of Fe₃O₄.

4. Molar volumes: Solid:
$$V_1 = \frac{58.5}{2.172} = 26.9334 \text{ cm}^3 \text{.mol}^{-1}$$

For liquid: $V_1 = \frac{58.5}{2.156} = 27.1336 \text{ cm}^3 \text{.mol}^{-1}$
Hence $\Delta V = 27.1336 - 26.9334 = 0.2002 \text{ cm}^3 \text{.mol}^{-1} \equiv 2.002 \times 10^{-7} \text{ m}^3 \text{.mol}^{-1}$
 $\frac{\Delta p}{\Delta T} = \frac{\Delta H_t}{\Delta V.T_t} \rightarrow \Delta H_t = \frac{(400-1)\times 1.013 \times 10^5 \times 2.002 \times 10^{-7} \times (801+273)}{0.32} = 27158 \text{ J.mol}^{-1}$

$$5. \frac{d \ln p}{dT} = \frac{184200 - 1.8T}{8.314T^2} \rightarrow \int_{1.013 \times 10^5}^{1.013 \times 10^6} d \ln p = \int_{1823}^{T} 22155.4T^{-2} - 0.2165T^{-1}dT$$
$$\ln 10 = -22155.4T^{-1} - 0.2165 \ln T - (-12.1532 - 0.2165 \ln 1823)$$
$$-22155.4T^{-1} - 0.2165 \ln T = -9.9425 \rightarrow T = 2266.5 \text{K} \equiv 1993.5^{\circ}\text{C}$$

6. There is one intermediate compound: ZrSiO₄ that decomposes above 1530°C to SiO₂ and ZrO₂ (ss).

Туре	Temperature °C	Reaction	% SiO2
Monotectic	2250	$Liquid = Liquid + ZrO_2 (ss)$	41
Eutectic	1670	$Liquid = SiO_2 + ZrO_2 (ss)$	97
Peritectoid	1530	$SiO_2 + ZrO_2 (ss) = ZrSiO_4$	0

There are three invariant points:

There is one intermediate compound: ZrTiO₄ (ss) that melts incongruently at 1830°C to liquid and ZrO₂ (ss). There are three invariant points:

Туре	Temperature °C	Reaction	% TiO ₂
Allotropic transition	2200	ZrO_2 (c) = Liquid + ZrO_2 (t)	35
Eutectic	1570	$Liquid = ZrTiO_4 (ss) + TiO_2 (ss)$	73
Peritectic	1830	$Liquid + ZrO_2 (t) = ZrTiO_4 (ss)$	60

8.



There are 3 intermediate compounds:

- Fe₂TiO₄ that melts congruently at 1395°C
- FeTiO₃ that melts incongruently at 1377°C giving off Fe₂TiO₅ and liquid
- FeTiO₅ that melts incongruently at 1455°C giving off TiO₂ and liquid There are five invariant points:

Туре	Temperature ^o C	Reaction	% TiO ₂
Eutectic	1312	$Liquid = FeO + Fe_2TiO_4$	14
Eutectic	1373	$Liquid = Fe_2TiO_4 + FeTiO_3$	44
Peritectic	1377	$Liquid + FeTi_2O_5 = FeTiO_3$	49
Peritectic	1455	$Liquid + TiO_2 = FeTi_2O_5$	64
Eutectoid	1150	$FeTi_2O_5 = FeTiO_3 + TiO_2$	0



9. There are four invariant points:

Туре	Temperature °C	Reaction	% CaO
Eutectic	618	$Liquid = V_2O_5 + CaV_2O_6$	8
Peritectic	778	$Liquid + Ca_2V_2O_7 = CaV_2O_6$	22
Peritectic	1015	$Liquid + Ca_3V_2O_8 = Ca_2V_2O_7$	36
Peritectic	1380	$Liquid + CaO = Ca_3V_2O_8$	47

Applying the ever arm principle, by trial, the required temperature is about 880°C.

SHEET 3: Kinetics of solid state reactions

1. $C(s) + \frac{1}{2}O_2(g) = CO(g)$

At the end of the reaction, ash is left, so that $\alpha = \frac{34.5 - 26.7}{34.5 - 0.87} = 0.232$ at t = 5 min. $t = \tau \left[1 - (1 - \alpha)^{1/3}\right] \rightarrow 5 = \tau \left[1 - (1 - 0.232)^{1/3}\right] \rightarrow \tau = 59.39$ min

2. $\alpha = 1 - e^{-Kt^2} \rightarrow 0.5 = 1 - e^{-17^2K} \rightarrow K = 0.002398 \rightarrow 0.99 = 1 - e^{-0.002398t^2}$ t = 43.8 min

3.
$$0.38 = 1 - e^{-24^{n_K}} \to 0.62 = e^{-24^{n_K}}$$
 $0.65 = 1 - e^{-72^{n_K}} \to 0.35 = e^{-72^{n_K}}$
 $-\ln 0.62 = 24^{n_K}$ and $-\ln 0.35 = 72^{n_K}$ Divide:
 $0.455 = \left(\frac{24}{72}\right)^n \to n = 0.72$

4. 2 WC (s) + 5 O₂ (g) = 2 WO₃ (s) + 2 CO₂ (g) (W = 184, C = 12, O = 16)
2 × (184 + 12)
$$\rightarrow$$
 2 × (184 + 3 × 16) \rightarrow 388 WC \rightarrow 464 WO₃
Hence, starting with 8.75 g WC, we get after full oxidation 10.357 g WO₃.
 $\alpha = \frac{9.8 - 8.75}{10.357 - 8.75} = 0.6533$
 $t = 74[(1 - 0.6533).\ln(1 - 0.6533) + 0.6533] = 21.17 \text{ min}$

5.
$$t = \tau [1 - (1 - \alpha)^{1/3}]^2$$
 (Mechanism D3)

Time min	1	4	9	17	30	48	75
Conversion	0.1	0.2	0.3	0.4	0.5	0.6	0.7
$[1-(1-\alpha)^{1/3}]^2$	0.00119	0.0051	0.0125	0.0245	0.0425	0.0692	0.1091

A plot of t vs $[1 - (1 - \alpha)^{1/3}]^2$ yields a straight line passing through origin of equation with $R^2 = 0.9999$:

$$t = 691.5[1 - (1 - \alpha)^{1/3}]^2 \rightarrow \tau = 691.5 \text{ min}$$

6. $-\ln(1-\alpha) = k.t$ (First order reaction)

Time min	5	10	15	40	60	70
Conversion	0.22	0.29	0.51	0.78	0.90	0.94
$-\ln(1-\alpha)$	0.248461	0.34249	0.71335	1.514128	2.302585	2.813411

A plot of $-\ln(1-\alpha)$ vs t yields a straight line passing through origin of equation with $R^2 = 0.9981$.

7.
$$t = \tau [1 - (1 - \alpha)^{1/3}]$$
 $\alpha = 0.9 \rightarrow t = \tau [1 - (1 - 0.9)^{1/3}] = 0.538\tau \approx 0.5\tau$

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$K.f(\alpha)$	3	2.8	2.56	2.25	2	1.77	1.42	1.1	0.71
$(1-\alpha)^{2/3}$	0.932	0.862	0.788	0.711	0.630	0.543	0.448	0.342	0.215

8. $f(\alpha) = 3(1 - \alpha)^{2/3}$ (R3 mechanism)

To prove that the reaction follows a R3 mechanism, plot $\frac{d\alpha}{dt} = K.f(\alpha)$ vs $(1 - \alpha)^{2/3}$. We should get a straight line passing through origin of slope = 3K. We get a straight line of equation $\frac{d\alpha}{dt} = 3.2186(1 - \alpha)^{2/3} \rightarrow K = 1.073 \text{ min}^{-1}$ (R² = 0.9999).

9. At a temperature = 260°C, $m_0 = 86$ mg, and at a temperature = 260°C, $m_0 = 45$ mg

Hence: $\alpha = \frac{86-m}{86-45} = \frac{86-m}{41}$

T ^o	260	270	280	290	300	310	320	330	340
С									
α	0.0000	0.0488	0.1463	0.2561	0.3902	0.6341	0.7805	0.9268	0.9762
$-\ln(1 - \alpha)$	0.0500	0.1582	0.2958	0.4947	1.0055	1.5163	2.6150	0.0500	0.1582
1/ <i>T</i> K ⁻¹	0.0018 4	0.0018 1	0.0017 8	0.0017 5	0.0017 2	0.0016 9	0.0016 6	0.0018 4	0.0018 1
$\ln g$ $/T^2$	15.590	14.474	13.884	13.406	12.731	12.354	11.843	15.590	14.474

A plot of $\ln g(\alpha)/T^2$ vs 1/T produces a straight line of slope = 19524.3 (R² = 0.9836) corresponding to an activation energy = **162.325 kJ.mol**⁻¹

10. A plot of $\ln \beta / T^2$ vs 1/T yields a straight line of slope = -19828.67 (R² = 0.9997) corresponding to an activation energy = **164**. **86** kJ.mol⁻¹

β	2	5	7.5	10
Τ°C	192.5	202	206.5	210
1/T K ⁻¹	0.0021482	0.0021053	0.0020855	0.0020704
$\ln \beta/T^2$	-11.59308	-10.71719	-10.33058	-10.05745

11. The following tables show the calculations

β	5	10	15	20					
α	T°C								
0.2	254.9	263.9	270.6	275.2					
0.3	271.4	280.3	287.1	292.5					
0.4	285.2	294.1	301.4	307.4					
0.5	297.1	306	313.8	320.2					
0.6	308	317.1	324.9	331.8					
0.7	319.3	328.4	336.1	343.8					
0.8	333.3	342.6	349.4	359.7					

$\log \beta$		0.69897	1	1.17609	1.30103	Slope	E kJ.mol- ¹	R ²
$1/T { m K}^{-1}$	0.2	0.00189	0.00186	0.00184	0.00182	-8549.5	155.64	0.997
	0.3	0.00184	0.00181	0.00179	0.00177	-8793.6	160.08	0.994
	0.4	0.00179	0.00176	0.00174	0.00172	-8781.4	159.86	0.990
	0.5	0.00175	0.00173	0.0017	0.00169	-8781.3	159.86	0.986
	0.6	0.00172	0.00169	0.00167	0.00165	-8880.7	161.67	0.984
	0.7	0.00169	0.00166	0.00164	0.00162	-8990.7	163.67	0.979
	0.8	0.00165	0.00162	0.00161	0.00158	-8798.5	160.17	0.956

11.

$1/T { m K}^{-1}$	0.2	0.00189	0.00186	0.00184	0.00182			
	0.3	0.00184	0.00181	0.00179	0.00177			
	0.4	0.00179	0.00176	0.00174	0.00172			
	0.5	0.00175	0.00173	0.0017	0.00169			
	0.6	0.00172	0.00169	0.00167	0.00165			
	0.7	0.00169	0.00166	0.00164	0.00162			
	0.8	0.00165	0.00162	0.00161	0.00158	Slope	<i>E</i> kJ.mol- ¹	R ²
$\ln \beta/T^2$	0.2	-10.928	-10.269	-9.888	-9.6175	-18610	154.73	0.997
	0.3	-10.99	-10.329	-9.9482	-9.679	-19139	159.12	0.993
	0.4	-11.04	-10.378	-9.998	-9.732	-19082	158.648	0.988
	0.5	-11.082	-10.420	-10.041	-9.775	-19057	158.44	0.984
	0.6	-11.120	-10.458	-10.079	-9.814	-19263	160.16	0.982
	07	11 150	_10/106	-10 116	-9.853	-19493	162.07	0.076
	U. /	-11.139	-1070	-10.110	7.055	17175	102.07	0.970