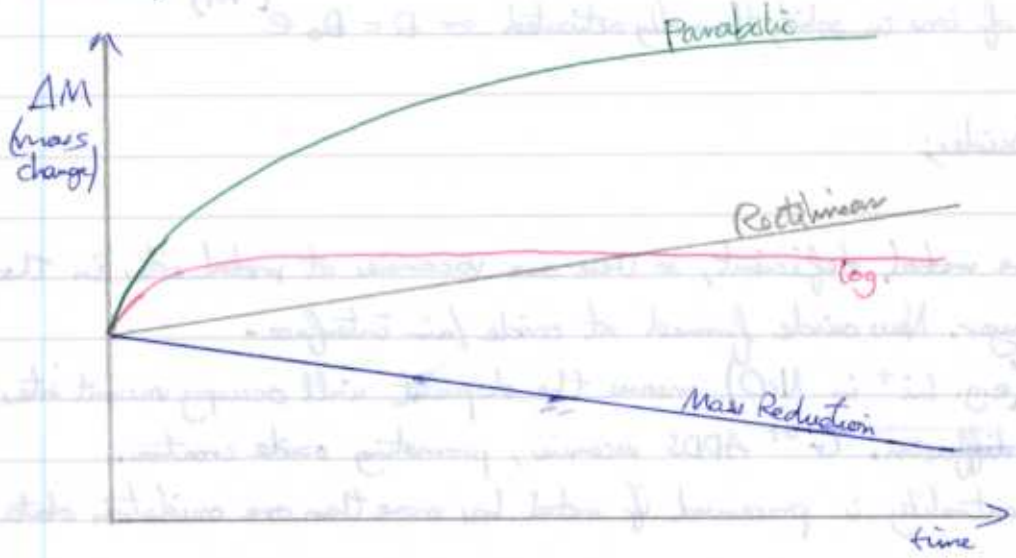
High-Temperature Oxidation of Metals;

* Metals are corroded by dry gases at high temps. Hot $O_2/H_2S/SO_2$ can react with the metal surface.
* Thermodynamics ⇒ Metal + O_2 → Metal Oxide generally favourable.
* Kinetics ⇒ affected by oxide layer.

Models;



* PARABOLIC (HIGH (T)); $-\frac{dm}{dt} = \frac{\text{constant}}{m}$ ∴ $(\Delta m)^2 = k_1 t$

  - oxide film covers surface, providing diffusional resistance.

* LOGARITHMIC (LOW (T)); $-\frac{dm}{dt} = k_1 \log(k_2 t + k_3)$

  - thin oxide provides complete protection from further oxidation once formed.

* RECTILINEAR; $-\frac{dm}{dt} = k_1$

⇒ Pilling-Bedworth (PB) ratio; relative vol. of oxide to pure metal.

PB < 1, oxide layer does not cover surface
PB ≥ 2, oxide layer contains cracks due to volume strain

* Mass loss can occur if oxide is volatile and is removed from the surface.

Parabolic Growth Rate Mechanism;

* $(\Delta m)^2 = kt$
* rate of oxide growth limited by ion diffusion through oxide layer.
* rate of oxide growth $\Rightarrow \frac{dx}{dt}$ or $D\frac{C_a}{x}$ $\therefore (\Delta x)^2 = kt$
* Diffusion of ions in solid; thermally activated so $D = D_0 e^{(-E/RT)}$

P-type Oxides;

* These are metal deficient, so there are vacancies at metal sites in the oxide layer. New oxide formed at oxide/air interface.
* Doping (e.g. Li^+ in NiO) means the dopant will occupy vacant site, reducing diffusion. Cr^{3+} ADDS vacancies, promoting oxide creation.
* Charge neutrality is preserved if metal has more than one oxidation state.

N-type Oxides;

* O^{a-} quicker than M^{n+} diffusion so oxygen ion diffusion dominate kinetics.
* Oxide layer forms at metal/oxide interface. This can cause tensile stress causing fracture of the oxide film.

Prevention;

* Dope oxide film
* Alloy metal so good film is produced.