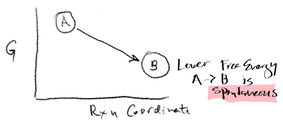
GIBBS FREE ENERGY

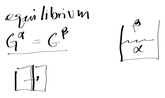
Thermodynamics treats the states & energies of substances

H – Enthalpy (Heat & Work)
S – Entropy (Disorder)
T – Temperature

$G = H - TS$ or $\Delta G = \Delta H^\circ - T\Delta S^\circ$



At equilibrium
$G^\alpha = G^\beta$



EXAMPLE 1

Is CH_4 compatible with O_2?

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

	CH_4	$2O_2$	CO_2	$2H_2O$	ΔG°
ΔG_f°	−50.8 (l)	0	−394	−237 (l)	= −818 kJ/mol
ΔH_{RXN}°	—	—	—	—	

$\Delta G^{products} < \Delta G^{reactants}$

$\sum$ Products − $\sum$ Reactants

EXAMPLE 2

Is Acetic Anhydride compatible with Sodium Hydroxide?
Check Gibbs or other ΔG for possible reactions

$$(CH_3CO)_2O + 2\,NaOH \longrightarrow 2\,CH_3COONa + H_2O$$

@ standard conditions

	$(CH_3CO)_2O$	$2NaOH$	$2CH_3COONa$	H_2O	ΔG°
$\Delta G_{f,DYNAM.}^\circ$	−954	−419	−607 (s)	−237	= −197 kJ/mol

- Check out chemical reaction possibilities using ΔG
- Check out chemical compatibility matrices with ΔG
- Remember Thermodynamics says nothing about rates of reaction
  → Kinetics

KINETICS & COMPATIBILITY

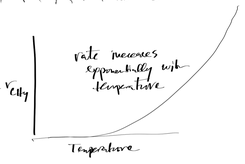
Arrhenius Equation

$k = A\exp(-E_a/RT)$

$CH_4 + O_2 \rightarrow$ Products

$r_{CH_4} = -k\,P_{CH_4}^a P_{O_2}^b$ [J] mol/sec

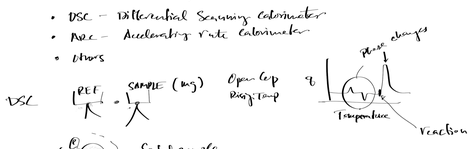
a,b order of reaction



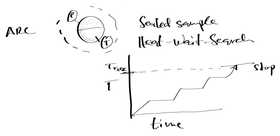
The temperature & some of the kinetic parameters can be found from calorimetry

- DSC – Differential Scanning Calorimeter
- ARC – Accelerating Rate Calorimeter
- Others

DSC



ARC



KINETICS & COMPATIBILITY

Are the process chemicals compatible?

CHEMICAL COMPATIBILITY MATRIX

	1	2	3	4
1	✓			
2	C	✓		
3	Y	N	✓	
4	N	N	C	SR

SR – self reactive
N – incompatible
Y – compatible
C – Caution

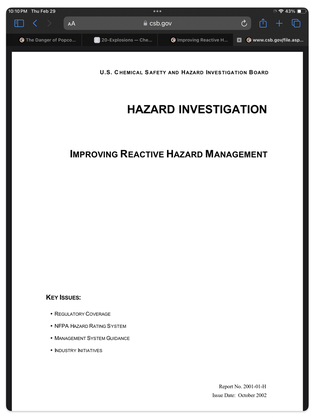
How could you find out if a lubricant for a pump shaft is compatible with the process chemical?

- SDS
- Chemical reactivity worksheet – Free NFPA program
- Literature: Bretherick's Handbook of Reactive Chemical Hazards
- Thermodynamics – Gibbs Free Energy
  $G = -RT\ln K$
  $K = \frac{[C][D]}{[A][B]}$
  $a + b \rightarrow c + d$

Chemical Reactivity

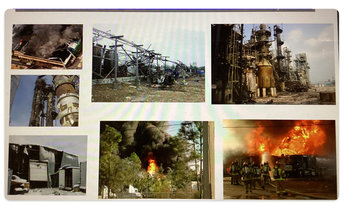
- Identify scenarios where chemical reactions may occur
- Gibbs free energy to determine driving force / reactivity → compatibility
- Use a chemical compatibility matrix
- Calorimeter introduction
- Understand Calorimeter data
- Kinetics introduction

REACTIVE CHEMICAL ACCIDENTS



Reactive Accidents from chemical reactions

- unseen chemical incompatibilities
- out-of-place chemical combinations
- run-away reactions
- process upset conditions



Even the CSB website – report is available

1167 Reactive Chemical accidents reviewed
108 fatalities

REACTIVE CHEMICAL GROUPS

- Azide $N{=}N{=}N^-\ Na^+$
- Diazo $-N{=}N-$ } unstable
- Nitro $-NO_2$
- Nitrite $-ONO$
- Nitrate $-ONO_2$
- Peroxide $-O-O-$
- Chlorate ClO_3
- Others

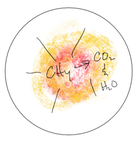
} Rich in oxygen

REACTIVE TYPES

- Pyrophoric (Zinc metal, Grignard reagent)
- peroxide formers
- water reactive (Na, Li, anhydride, strong acid/bases)
- Oxidizers (HNO_3, thermite, etc)
- self-reactive (Nitrocellulose, auto catalytic)
- Incompatible materials

See Appendix D for Examples

In Class Discussion



Combustion Inside Closed Container

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
3 mol → 3 mol

$r_{CH_4} = -k P_{CH_4}^a P_{O_2}^b$ or as an approximation
$r_{CH_4} = -k$

Mole Balance

total: $\frac{dn}{dt} = 0$ for stoichiometric mixture adiabatic isobaric (ideal gas)
since 3 mol in → 3 moles
also assuming the water stays in the vapor phase

Energy Balance

$\frac{dnU}{dt} = gen = +k\,\Delta H_{rxn}$ [J] $\frac{mol\ CH_4}{sec} \cdot \frac{J}{mol\ CH_4}$ [J] $\frac{J}{sec}$

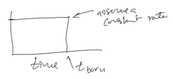
could include heat losses to surroundings $q \sim hA(T - T_0)$ or $\sigma\epsilon A(T^4 - T_0^4)$ radiation

$n\frac{dU}{dt} + U\frac{dn}{dt}^{0} = nC_v\frac{dT}{dt} \rightarrow nC_v\frac{dT}{dt} = k\,\Delta H_{rxn} \rightarrow \Delta H_{rxn}\int_0^t k(time)\,dt = nC_v(T_f - T_i)$

↗ If k is considered a constant with respect to temperature

Ideal Gas: $PV = nRT$
Can solve above conditions for n (constant) & T (changing) with V constant to get P as a f(time), including P_{max} and impulse

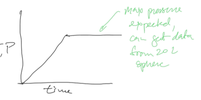
Example: Give $k_r(time)$ =



$T_i + \frac{\Delta H_{rxn} \cdot k\,t}{nC_v} = T$ ← temperature of gases in volume

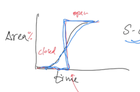
k – estimated constant burn rate; t – time up to t_{burn}

$P = \frac{nR}{V}\left[T_i + \frac{\Delta H_{rxn} \cdot k\,t}{nC_v}\right]$



Add Vent

What if the pressure expected is greater than the rating for the vessel?
↳ venting, burst disk, fast acting



S-curve: $\frac{1}{1 + e^{-at+5}}$ ← Mimics the opening dynamics of the burst disk; a – rate of increase

opening time, 67% open $= \frac{5.708}{a}$

$0.67 = \frac{1}{1+e^{-at+5}}$ $\quad 0.67\,e^{-at+5} = 1 - 0.67 = 0.33$

$e^{-at+5} = \frac{0.33}{0.67} =$

$-at + 5 = \ln\left(\frac{0.33}{0.67}\right) = -0.708$

$t_{open} = 5.708/a$ or $a \propto$ massing vent (proportional)

So, vent area is a function of time:

$a = \frac{5.708}{t_{open}}$ → 67% open

$A = A_{fo} \cdot \frac{1}{1+e^{-at+5}}$ $\quad t = 0$ when P equals the set pressure of the relief

A_{fo} – fully open area

$\frac{dn}{dt} = \cancel{\dot{n}_{in}}^{0} - \dot{n}_{out} + \cancel{gen}^{0} \rightarrow \frac{dn}{dt} = -\dot{n}_{out}$

$\frac{dnU}{dt} = n\frac{dU}{dt} + U\frac{dn}{dt} = \cancel{\dot{n}_{in}\bar{H}_{in}}^{0} - \dot{n}_{out}\bar{H} + \Delta H_{rxn}\,r\,V$

assume constant properties for simplicity

$H = U + PV$ for ideal gas
$H = U + RT$

$nC_v\frac{dT}{dt} = +\bar{U}\dot{n}_{out} - \dot{n}_{out}\bar{H} + \Delta H_{rxn}\,r\,V$

$= (\bar{U} - \bar{H})\dot{n}_{out} + \Delta H_{rxn}\,r\,V$

$nC_v\frac{dT}{dt} = -RT\dot{n}_{out} + \Delta H_{rxn}\,r\,V$

$\dot{n}_{out}$ = gaseous flow equation with the Area equal to 0 if $P < P_{burst\ disk}$

$A_{fo} \cdot \frac{1}{1+e^{-at+5}}$ if $P > P_{burst\ disk}$
where $t = 0$ when $P = P_{burst\ disk}$

Combustion of Fuel inside Closed Container

K_{FS} – fluids $\quad \frac{dP}{dt}\Big|_{evap} \cdot V^{1/3}$

K_G – gases

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
3 moles → 3 moles

total mole b. $\frac{dn}{dt} = 0$ no vent, not produced moles

$$\frac{d(U + \cancel{K} + \cancel{PE})}{dt} = \sum_{inlets}\dot{n}\left(H + \frac{V^2}{2} + gz\right) - \sum_{outlets}\dot{n}\left(H + \frac{V^2}{2} + gz\right) + \dot{Q}_{cv} + \dot{W}_{cv}^{0}$$

control volume not moving; accum; usually much lower than enthalpy (H) terms

Energy b.: $\frac{dn\bar{U}}{dt} = \cancel{\dot{n}_{in}}^{0} - \cancel{\dot{n}_{out}} + gen$

gen: $r_{CH_4} = k$ ← constant $\quad k = Ae^{-E_a/RT}$

$\frac{mol}{sec \cdot m^3}$

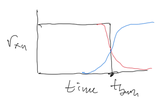
$\frac{dn\bar{U}}{dt} = +k \cdot \Delta H_{rxn} \cdot V$ [J] $\frac{J}{mol} \cdot \frac{mol}{sec \cdot m^3} \cdot m^3 \cdot \frac{J}{mol}$

$k = \frac{1}{sec \cdot m^3}$

$\Delta H_{rxn} = \sum H_{prod}^\circ - \sum H_{react}^\circ$

$\frac{dn\bar{U}}{dt} = n\frac{d\bar{U}}{dt} + \bar{U}\cancel{\frac{dn}{dt}}^{0}$

$n\frac{d\bar{U}}{dt} = k \cdot \Delta H_{rxn} \cdot V$



$\bar{U} = C_v(T - T^\circ)$

$\frac{d\bar{U}}{dt} = C_v\frac{dT}{dt}$ Assuming C_v constant

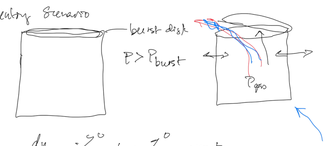
$nC_v\frac{dT}{dt} = k\,\Delta H_{rxn} \cdot V$

$P_{(t)} = \frac{nRT(t)}{V}$ $\quad \frac{dT}{dt} = \frac{k\,\Delta H_{rxn} V}{nC_v} \cdot$ sigmoid

$T(t)$

Add Vent

Venting Scenario



$\frac{dn}{dt} = \cancel{\dot{n}_{in}}^{0} - \dot{n}_{out} + \cancel{gen}^{0} = -\dot{n}_{out}$

$\dot{n}$ – gases flowing through an orifice

$= PA\,Ma\sqrt{\frac{\gamma}{RT\,M_w}}\left(1 + \frac{\gamma - 1}{2}Ma^2\right)^{-\frac{\gamma+1}{2(\gamma-1)}}$

Ideal Gas $P = nRT/V$

Energy Balance $\frac{dn\bar{U}}{dt} = \cancel{\dot{n}_{in}\bar{H}_{in}}^{0} - \dot{n}_{out}\bar{H} + gen$ $\quad rV \cdot \Delta H_{rxn}$