

GIBBS FREE ENERGY

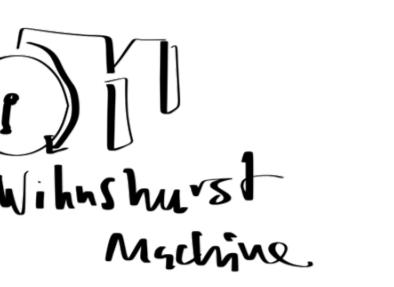
Thermodynamics treats the states + energies of substances

H - Enthalpy (Heat + Work)

S - Entropy (Disorder)

T - Temperature

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



Class 1 Items

- Spontaneous - Peony's Power (Res. Reactions or Rupture)
- Monitors for Mid course evaluations
- Static Electricity hazards & demo
 - 3 kV/mm
 - Corona discharge
 - Spark discharge
 - What is the voltage of spark?
 - What is the energy of the spark?
 - Capacitance $C = \frac{Q}{V}$

Chemical Reactivity

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

REACTIVE CHEMICAL ACCIDENTS

Thu Feb 29 10:10 PM

[AA](#) [csb.gov](#) [B](#) [D](#) [E](#) [F](#) [G](#) [H](#) [I](#) [J](#) [K](#) [L](#) [M](#) [N](#) [O](#) [P](#) [Q](#) [R](#) [S](#) [T](#) [U](#) [V](#) [W](#) [X](#) [Y](#) [Z](#)

The Danger of Pe... 20-Explosions - Che... Improving Reactive H... www.csb.gov/file.asp...

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

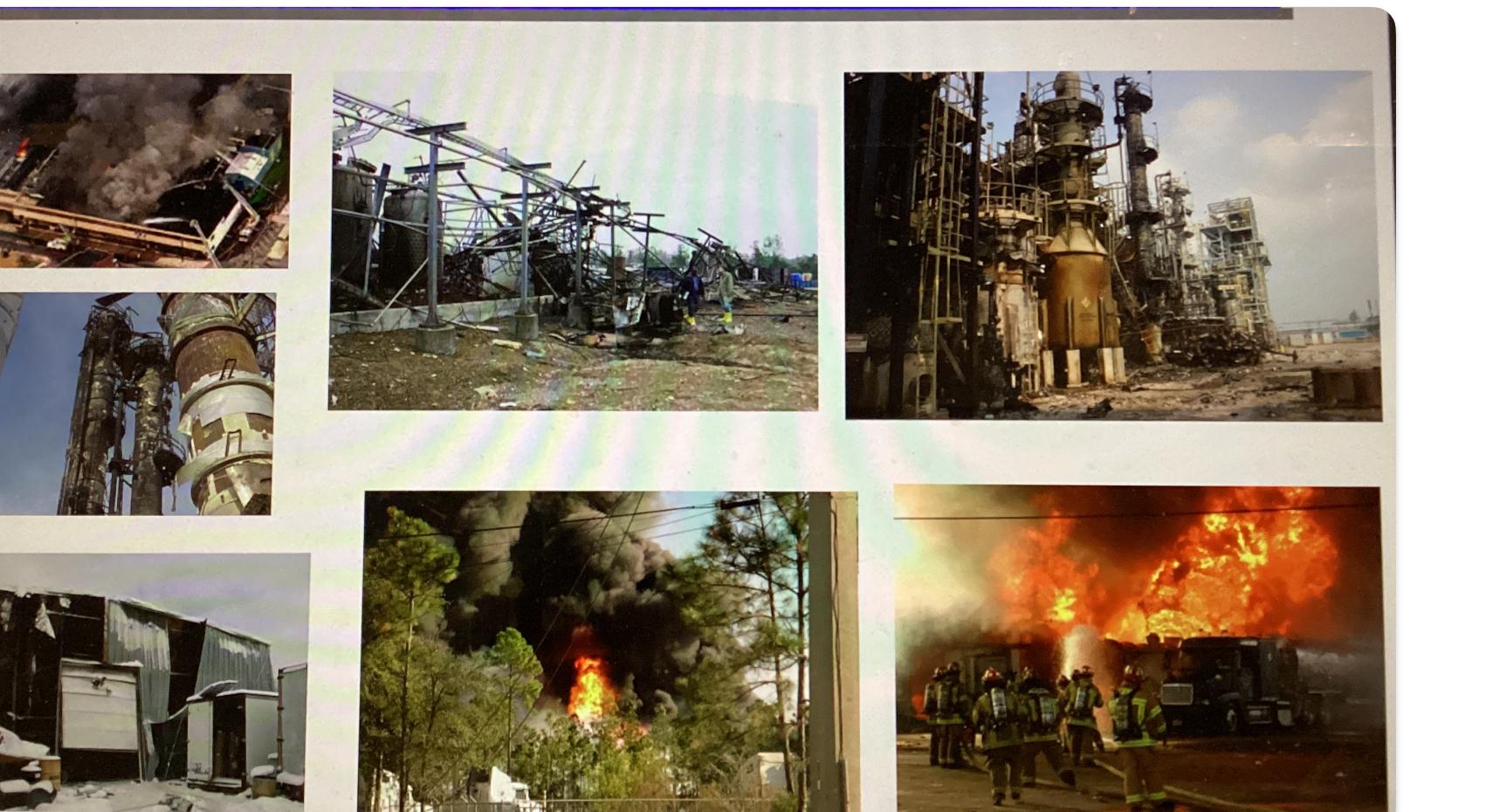
HAZARD INVESTIGATION

IMPROVING REACTIVE HAZARD MANAGEMENT

KEY ISSUES:

- REGULATORY COVERAGE
- NFPA HAZARD RATING SYSTEM
- MANAGEMENT SYSTEM GUIDANCE
- INDUSTRY INITIATIVES

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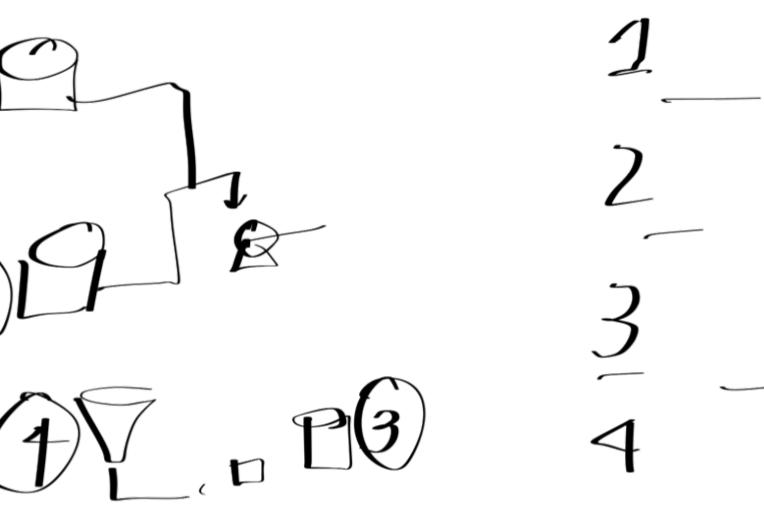


From the CSB website - report is available

167 reactive chemical accidents reviewed
108 fatalities

REACTIVE CHEMICAL GROUPS

- Azide $N=N=N$
- Diazo $-N=N-$
- Nitro $-NO_2$
- Nitrite $-ONO$
- Nitrate $-ONO_2$
- Peroxide $-O-O-$
- Chlorate ClO_3^-
- Others



Are the process chemicals compatible?

CHEMICAL & COMPATIBILITY MATRIX

	1	2	3	4
1	V	I	I	I
2	C	V	I	I
3	V	I	V	I
4	N	I	C	SR

Legend:
 V - Very reactive
 I - Inert
 C - Compatible
 SR - Self reactive
 N - Incompatible

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

- SDS
- Chemical reactivity worksheet
 - Free ARCEC program
- Literature:
 - Bretherick's handbook of reactive chemical hazards
- Thermodynamics
 - Gibbs Free Energy
 - $G = -RT\ln K$
 - $K = \frac{[C][D]}{[A][B]}$
 - $a + b \rightarrow c + d$

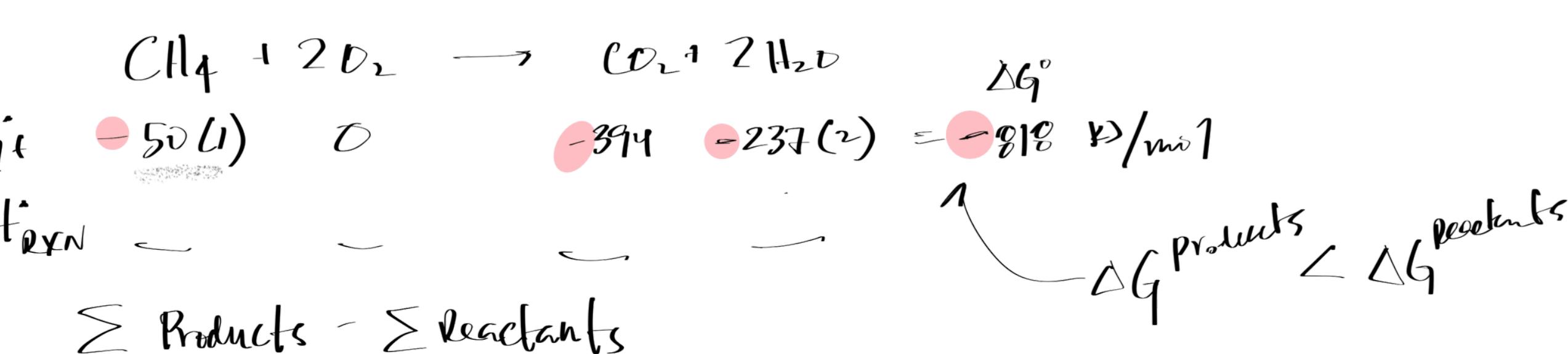
REACTIVE TYPES

- Pyrophoric (live metal, Grignard reagent)
- peroxide formers
- water-reactive (Na, Li , anhydride, strong acid/bases)
- oxidizers (H_2O_2, H_2O_3 , etc.)
- self-reactive (nitrocellulose, azobisisobutyric)
- Incompatible materials

See Appendix D for Examples

EXAMPLE 1

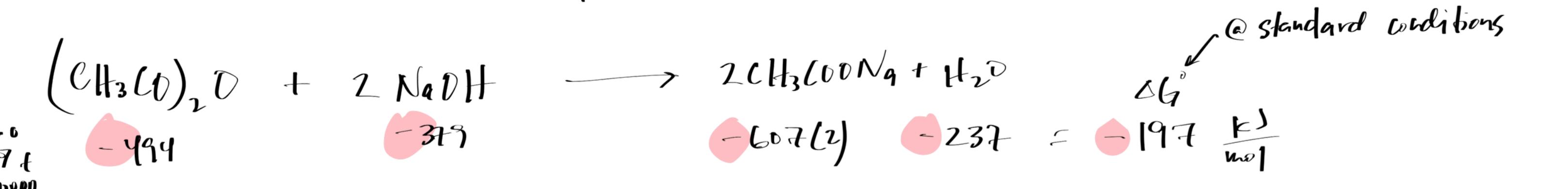
Is CH_4 compatible with O_2 ?



EXAMPLE 2

Is Acetic Anhydride compatible with Sodium Hydroxide?

Check Gerkin or other AI for possible reactions



- Check out chemical reaction possibilities using AT
- Check out chemical compatibility matrices with AI
- Remember Thermodynamics says nothing about rates of reaction

↳ Kinetics

KINETICS & COMPATIBILITY

Arrhenius Equation:

$$k = A e^{-E_a/RT}$$



$$\ln k = -E_a/RT + \ln A$$

$$\ln k = -E_a/RT + \ln A$$

rate increases exponentially with temperature

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

- DSC - Differential Scanning Calorimeter
- ARC - Accelerating Rate Calorimeter
- DSCs

