Thermodynamics

[1]**Safety Module 1:** *Praxair Flammable Gas Cylinder Explosion, June 24, 2005, in St. Louis, MO*

Problem Statement: It was a hot day in St. Louis, 96°F (35.9°C), where Praxair had set cylinders with flammable gases on hot black asphalt pavement. Direct sunlight and radiant heat from the asphalt pavement[2†] heated the propylene cylinders.

The vapor pressure in a liquid propylene cylinder exceeded a faulty set pressure on the cylinder's relief valve that was too low, and propylene escaped into the yard. The resulting vapor plume found an ignition source and a fire started. The fire heated nearby acetylene and liquefied petroleum gas (LPG) cylinders and they in turn released more flammable gases, which enlarged the fire.

Pressure relief valve – cut away

Watch the Video: (*https://www.youtube.com/watch?v=-_ZLQkn7X-k*)

Incident Report Available At: (*https://www.csb.gov/file.aspx?DocumentId=5642*) (pages 1-10)

(a) It is important that chemical engineers understand what the accident was, why it happened and how it could have been prevented in order ensure similar accidents may be prevented. Applying a safety algorithm to the accident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, view the Chemical Safety Board video on the Praxair flammable gas fires and explosion and fill out the following algorithm. See definitions on the last page. If necessary, view pages 1-10 of the incident report.

Safety Analysis of the Incident

Activity: ____

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Hazard: ____

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[1] In collaboration with Kara Steshetz, University of Michigan and Professor Andrej Lenert, University of Michigan

[2†]Katharine K. Guan, "Surface and ambient air temperatures associated with different ground material: a case study at the University of California, Berkeley, *"Surface and Air Temperatures of Ground Material* Spring 2011.310

Incident: ______________________

Initiating Event: ______________________

Preventative Actions and Safeguards: ______________________

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Contingency Plan/ Mitigating Actions: ______________________

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Lessons Learned: ______________________

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On the day of the explosion, the air temperature reached 97°F (36°C) at 2 p.m. and the asphalt surface was approximately 140°F (333 K) causing the cylinder temperature to be at least 135°F (330 K).

Additional information:

Propylene boils at 225.6K at 1 atm (101.3 kPa). The heat of vaporization is 18.4 kJ/mol R = 8.314 J/mol•K, the critical pressure and temperature are P_C = 4.6 MPa and T_C = 364.9 K respectively, and the vapor molar volume of propylene is $2.13 \cdot 10^{-3}\ \frac{m^3}{mol}$

(b) Use the ideal gas law to estimate the pressure, P, inside the cylinder at 25°C and at 57°C (330 K) when there is only propylene gas.

(c) Assuming vapor liquid equilibrium estimate the pressure, P, in the cylinder at 25°C and at 57°C using

(1) The Clausius-Clapeyron equation

$$\boldsymbol{P}_2 = \boldsymbol{P}_1 \exp\left[\frac{-\Delta \boldsymbol{H}_{vap}}{\boldsymbol{R}}\left(\frac{1}{\boldsymbol{T}_2} - \frac{1}{\boldsymbol{T}_1}\right)\right]$$

(2) The short cut equation

$$\log_{10}\left(\frac{\boldsymbol{P}}{\boldsymbol{P}_C}\right) = \frac{7}{3}(\omega + 1)\left(1 - \frac{\boldsymbol{T}_C}{\boldsymbol{T}}\right)$$

Where ω is the acentric factor[3,4] with ω = 0.142 for propylene.[5]

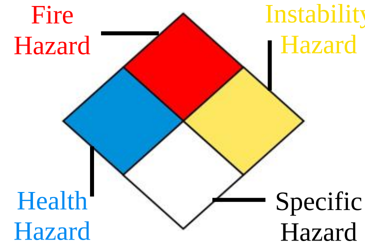
[3] Dahm, K.D. and D. P. Visco, *Fundamentals of Chemical Engineering Thermodynamics*, p.311, Cengage Learning, Stamford, CT (2015).

[4] Matsoukas, T., *Fundamentals of Chemical Engineering Thermodynamics with Applications to Chemical Processes*, p.49, Prentice Hall, Upper Saddle River, NJ (2013).

[5] Propylene properties see: https://webbook.nist.gov/cgi/cbook.cgi?ID=C115071&Mask=4

(d) Plot Pressure, P, as a function of Temperature, T, using the ideal gas law, the Clausius-Clapeyron equation and the short cut equation from 25°C to 67°C on the same figure and then write a conclusion.

(e) Review the information in the NFPA Diamond tutorial. After reviewing the information, visit the CAMEO Chemicals website and fill out the blank NFPA Diamond to the right for propylene.

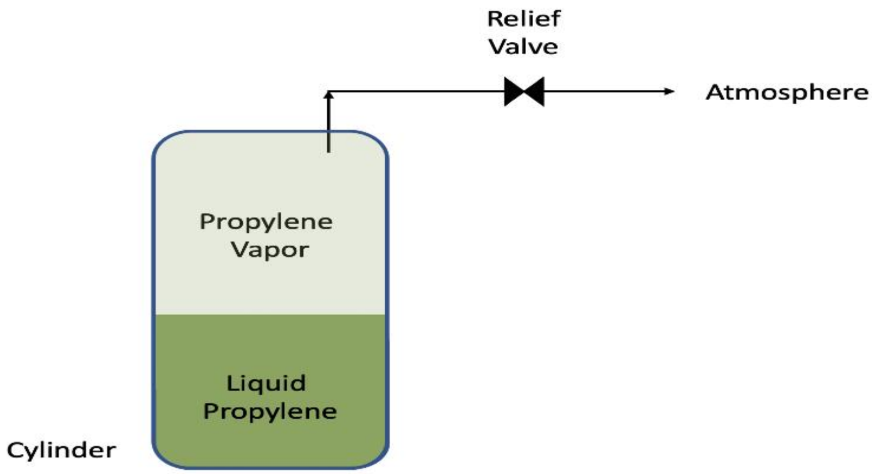


Parts (f)-(h) are based on industry practices used to assess process safety. For more information on process safety and its importance in chemical engineering, please visit the University of Michigan SafeChE website here. *It is recommended that professors only assign 1-2 of the following parts due to the similar nature of the questions.*

(f) Review the explanation of the components of a BowTie diagram found here. After reviewing the information, create a BowTie diagram for the Praxair incident.

(g) A HAZOP study is structured analysis of process design to identify potential vulnerabilities in a facility. Review the background on how to conduct a HAZOP study here before completing one for the following system. It is important to note that not all guidewords and parameters will be relevant for different systems. Some information is given here for guidance:

System to consider: Praxair cylinder filled with propylene in vapor-liquid equilibrium



Process Parameters to Consider: Temperature, Pressure

(i) Fill out the HAZOP chart as shown in the tutorial. In this case, the consequences, safeguards, and recommendations will be the same for both deviations.

Guideword + Parameter = Deviation	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
More (Higher) Temperature				
More (Higher) Pressure	Increase of temperature in cylinder			

(ii) When conducting a HAZOP, you will often find combinations of guidewords and parameters that describe a possible situation for the system that is not hazardous. For the given process parameters, give an example and explain why the situation is not hazardous.

(iii) Write a short conclusion on some takeaways from completing a HAZOP for this system and recommendations you would make.

(h) A Layers of Protection Analysis (LOPA) is a semi-quantitative study to identify available safeguards and determine if the safeguards sufficiently protect against a given risk. Review the background on how to conduct a LOPA study here before filling the table out for the system described in this module. Some information is given for guidance:

- Assume that the plant can only accept a minor risk
- The fire destroyed many cylinders and tanks, resulting in business losses of more than $100,000. Flying cylinders created the potential for severe injuries
- The ultimate cause of the incident was the heat wave, which can be expected to occur 1 time every year in St. Louis

LOPA Study for Praxair Fire and Explosion		
Initiating Event	Cause:	Heat wave
	Consequence:	Release of propylene vapor due to high pressure in cylinder and potential for ignition and explosion
	FOIE:	
IPL(s)	Description of IPL_1, IPL_2, ...	
	PFD = PFD_1 x PFD_2 x ...	
MCF	MCF = FOIE x PFD	
	Category of MCF:	
Severity	Impact:	Potential for severe injury and some business losses
	Category:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	
If risk evaluated above is unacceptable, please continue below:		
Proposed IPL(s) (P-IPL(s))	Description of $P\text{-}IPL_1$, $P\text{-}IPL_2$, ...	
	P-PFD = $P\text{-}PFD_1$ x $P\text{-}PFD_2$ x ...	
MCF	MCF = FOIE x PFD x P-PFD	
	Category of MCF:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	

(i) Describe what was the most unsettling to you about the incident.

Wolfram

Click here to download Wolfram CDF Player for free.

Click here to view CDF installation tutorial.

Click here to download Wolfram code for this module.

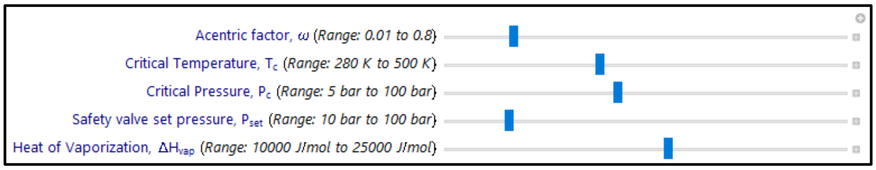


Fig 1.1 Wolfram Sliders

Wolfram graph:

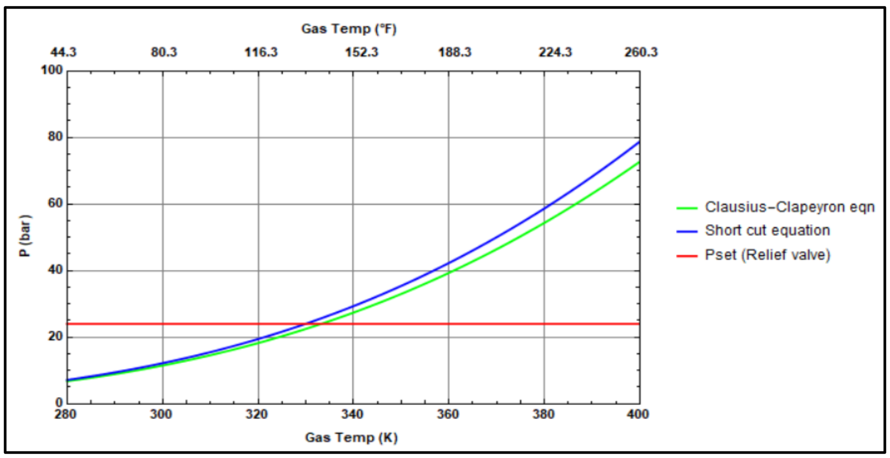


Fig 1.2: Vapor pressure vs. temperature

(i) Refer to the Wolfram plot of vapor pressure vs. temperature obtained using the shortcut equation. Find the minimum set pressure such that the explosion could have been prevented. Assume that the explosion occurred at a temperature of 135°F (330 K). Vary the slider for set pressure and describe how maximum allowable temperature varies with increasing set pressure.

(ii) What is the required set pressure if you use the Clausius Clapeyron Equation with ΔH_{vap}=15 kJ/mol? Is this set pressure more or less than that obtained in (i). Vary the ΔH_{vap} slider to check at what value of ΔH_{vap} the Clausius Clapeyron Equation agrees with the shortcut equation (within 3%). Can you explain the discrepancy between the pressures calculated by the two equations?

(iii) Describe how the vapor pressure – temperature curve (for shortcut equation) changes when propane is changed to butane or ethane. Vary the sliders for P_{set} and describe what you find. Are there any generalizations that you can make? Keep in mind that the Wolfram plot is generic and shows entire temperature range, but the curves for different substances will not be valid past their critical temperature.(*Hint: use the additional information below)*

(iv) Write a set of conclusions based on your experiments (i) through (iii).

Additional information:
Shortcut equation parameters-
Ethane:
T_c=305.4 K, P_c=48.8 bar, ω=0.099
Butane:
T_c= 425.2 K, P_c= 38.0 bar, ω= 0.199

Table 1.1: Nomenclature

Symbol	**Description**	**Unit**
T_c	Critical temperature	K
P_c	Critical pressure	bar
ω	Acentric factor	---
ΔH_{vap}	Enthalpy of vaporization	kJ/mol

Definitions

Activity: The process, situation, or activity for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property, or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to property, harm to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g., failure of equipment, instrumentation, human actions, flammable release, etc.). Could also include precursor events, (e.g., no flow from pump, valve closed, inadvertent human action, ignition). The root cause of the sum events in causing the incident.

Preventative Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property, or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/ Mitigating Actions: These actions occur after the initiating event. They are steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

BowTie Diagram: A qualitative hazard analysis tool through which potential problems and consequences associated with a hazard are studied through a pictorial representation. Necessary preventive and mitigating barriers are determined to reduce the process safety risk.

Hazard and Operability Study (HAZOP): A qualitative hazard analysis tool that uses a set of guide words to determine whether deviations from design or operating intent can lead to undesirable consequences. The existing safeguards are evaluated and if required, actions are recommended to mitigate the consequences.

Layer of Protection Analysis (LOPA): A semi-quantitative study that determines initiating event frequency, consequence severity, and likelihood of failure of independent protection layers (IPLs) to calculate the risk of a scenario. If the existing risk is intolerable, then additional IPLs are suggested to bring down risk to an acceptable level.

Module Specific for Praxair Cylinder Fire and Explosion

Set Pressure: Pressure at which a relief valve begins to open

Relief Valve: A spring-operated valve designed to prevent damage to equipment due to high pressure