

Vapor-Liquid-Equilibrium

Virtual PVT Phase Behavior Cell

SOPE – Simulation Of Phase Equilibria

1. INTRODUCTION

This program allows you to do accurate PVT EXPERIMENTS in a fraction of the time that would take to do it in the real lab. You will still learn the problems associated with the real experimentation but using a ‘virtual and safe reality’.

You have a vessel that you may fill with one or two components. These may be selected from SOPE's component library, as we will see later.

In this virtual PVT cell, you can set the temperature and either you fix the volume or you specify the pressure by putting weights on a piston. You cannot specify the three PVT!!! That is

Specified	Observed
Pressure, Temperature, amount of component(s)	Volume Single or Two-Phases (Gas and liquid) Phase compositions
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You can observe the phase equilibrium in the vessel and see how it changes when you alter the composition, the temperature or the pressure.

For any action, the strike of a SINGLE KEY is sufficient

The ONLY way to alter the value of a parameter is by the ARROW UP and ARROW DOWN key.

The selected parameter is then increased (arrow up) or decreased (arrow down) by the amount shown at the BOTTOM LINE of the screen

2. SET UP DESCRIPTION

When you start the virtual cell you will see your experimental equipment on the screen. It consists of a PVT cell with a movable piston, a pressure meter, a thermometer and two vessels that may contain two different substances, each one equipped with a molemeter that tells you how much mass you added to the PVT cell. (The molemeter does not tell you the moles in the vessel but the moles added to the PVT cell). The measurement is provided in millimols (1 millimol = 1/1000 moles).

The PRESSUREMETER left of the vessel has a readout in bar with the number of 100 units indicated in the center. For example, if the hand points at 75 and the center digit is a 2, then the pressure in the vessel is 275 bar (approximately 275 atmospheres)

Please note that the vessel has been designed to withstand pressures up to 850 bar; be careful not to blow the cell in your experimentation.

The readout of the THERMOMETER is in Kelvin. Degrees Centigrade can be obtained by subtracting 273.

The MOLEMETERS under the stocks show the number of millimoles of molecules of the respective substances in the vessel.

Basically, you can do TWO types of experiments:

- Experiments at specified temperature and pressure.
- Experiments at specified temperature and volume.

You may change the pressure by putting weights on the piston. Your cell is not equipped with a device to alter the volume, but the volume may be fixed at the present value by fixing the piston at its present position.

Simulations may be performed on **PURE** component or on **BINARY** mixtures with a large selection of choices for the components.

These are SIMULATIONS of real experiments using an EQUATION OF STATE. This program offers the possibility to use different equations of state for the simulations. The simplest, but highly inaccurate, choice is the well-known ideal gas law. The other choices follow a historical development up to the "CUBIC-4G" equation of state that may be considered as the present state of the art.

3 KEY FUNCTIONS

The following keys can be used to control the operation of the virtual cell.

- t :** Alter the **t**emperature.
- w :** Alter the **w**eight on the piston.
- n :** Alter the **n**umber of molecules in the vessel.
- v :** Use fixed/**v**ariable cell **v**olume by locking/unlocking the piston at present **p**osition.
- c :** Select another **c**omponent (or other components) from a menu.
- d :** Digital readout of the thermodynamic state on/off
- r :** Repair the set up (useful when you blew it up)
- h :** A quick look at the most important key functions.
- i :** More comprehensive **i**nformation on the program.
- k :** Introduce or alter a binary interaction coefficient **k**(1,2).
- 1 :** Work with **1** component (unary system).
- 2 :** Work with **2** components (binary system).

- +** : Increase the step size of the presently selected parameter.
- : Decrease the step size of the presently selected parameter. Step sizes are shown **a**t the bottom line of the screen.

Arrows

- UP:** Increase the selected parameter.
- DOWN:** Decrease the selected parameter.
- RIGHT:** Select another parameter that is shown right of the present parameter at the bottom lines.
- LEFT:** Select another parameter that is shown left of the present parameter at the bottom lines.
- Esc :** Pressing the ESCAPE key only has effect in a menu or in a help screen. It will always bring you to SOPE in the state it was in when you invoked the menu or the help screen
- q :** You want to quit SOPE.

4. DIGITAL OUTPUT DESCRIPTION

If you type "d", then the upper part of the screen will show you some NUMERICAL information on the present phase equilibrium in the vessel.

Such a panel could typically look like this for, say, a mixture of 40 millimoles of methane and 40 millimoles of butane

```
Temp. :10.0 °C
Pres.  :34.96 bar
Vol.   :22.54 cc
Num.   :80 millimol      Phase : vapour-liquid EoS : CUBIC-4G
MolarVol : 582.5 cc/mol (80.8 %)   CH4 : 92.7 %
        88.7 cc/mol (19.2 %)     CH4  22.6 %
```

(a demonstration will be conducted in the lab)

5. COMPONENTS

SOPE offers a choice from of the following 27 components.

INORGANICS	HYDROCARBONS	
	SATURATED	UNSATURATED
Hydrogen (H ₂)	Methane (CH ₄)	Ethylene (C ₂ H ₄)
Nitrogen (N ₂)	Ethane (C ₂ H ₆)	Propylene (C ₃ H ₆)
Carbon dioxide (CO ₂)	Propane (C ₃ H ₈)	Butene-1 (C ₄ H ₈)
Hydrogen Sulfide (H ₂ S)	n-Butane (C ₄ H ₁₀)	Benzene (C ₆ H ₆)
Argon (Ar)	n-Octane (C ₈ H ₁₈)	Toluene (C ₇ H ₈)
Oxygen (O ₂)	i-Butane (C ₄ H ₁₀)	Cyclohexane (C ₆ H ₁₂)
Carbon monoxide (CO)	i-Pentane (C ₅ H ₁₂)	Acetylene (C ₂ H ₂)
	n-Pentane (C ₅ H ₁₂)	Propyne (C ₃ H ₄)
	n-Hexane (C ₆ H ₁₄)	Propadiene (C ₃ H ₄)
	n-Heptane (C ₇ H ₁₆)	
	n-Decane (C ₁₀ H ₂₂)	

6. EQUATIONS OF STATE

The phase equilibrium in the vessel is calculated by the means of an equation of state. The calculation is performed after each change in one of the system variables, i.e. the component(s), the number of moles (n), the temperature [T], and - only if the volume [V] is (dependent) variable - the pressure[p].

Models do not substitute experimental data, but sometimes they are used when no data are available or too expensive to obtain and their predicted properties have an expected and tolerable degree of inaccuracy. Additionally, many of these models have been developed (or calibrated) to experimental data. We will discuss the use of models later on in the course.

Besides 1) the ideal-gas EOS ($pV=nRT$), merely introduced for reference purposes, the following cubic (in V) equations of state are available

- 2) Van der Waals (1873),
- 3) Redlich-Kwong (1949)
- 4) Soave-Redlich-Kwong (1972),
- 5) Peng-Robinson(1976)
- 6) CUBIC-4G (1988, a generalized 4-parameter form developed at KSLA)

NOTE: Unless specifically introduced, NO binary interaction coefficients are used in the mixing rules of the parameters present in these EOS.

A value for the binary interaction coefficient $k(1,2)$ in the mixing rule for

$$a(1,2) = \text{SQRT}[a(1,1)*a(2,2)] * [1-k(1,2)]$$

can be entered by typing “k” Changing the equation of state will reset $k(1,2) = 0.0$

You will use this virtual PVT cell to:

1. Determine the vapor pressure of a substance.
2. Determine the z-factor of a substance.
3. Analyze the effects of sample size, sample impurities, and leaks on your measurements.
4. Determine bubble points and dew points of a binary mixture (phase envelopes).

Have Fun