### **Review of Separation Principles**

# An hour in the library could save you six weeks in the laboratory.

George Quarderer

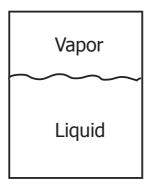
Mixer and Splitter Reactor Flash Distillation Absorption Mixer and Splitter Reactor Flash Distillation Absorption

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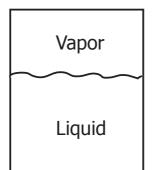
Before we develop linear models for flash and distillation units, we will review some fundamental principles of separations that were covered in previous courses.

- 1. Pure Substance
- When a pure liquid is placed in a sealed container, part of the liquid evaporates.



#### 1. Pure Substance

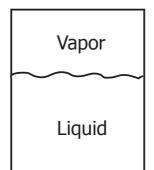
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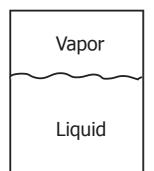
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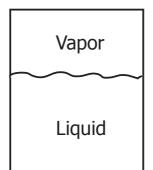
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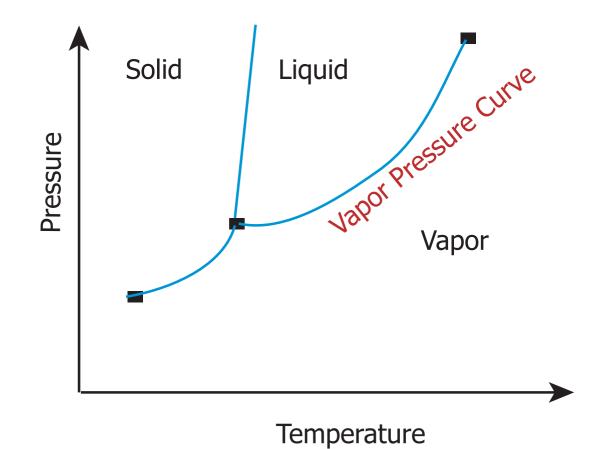
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- The value of the vapor pressure is independent of the amount of liquid in the container.
- Vapor pressure increases with temperature.

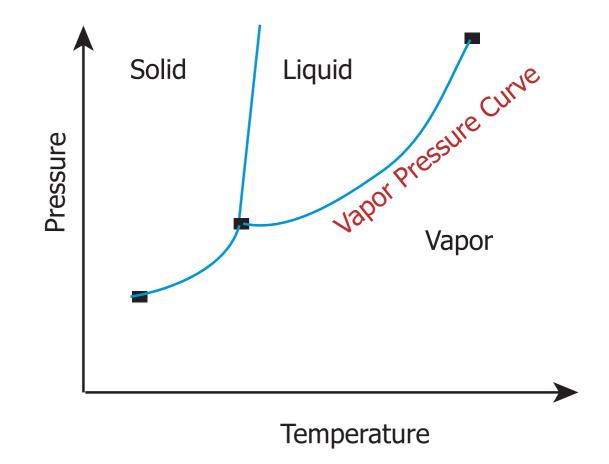
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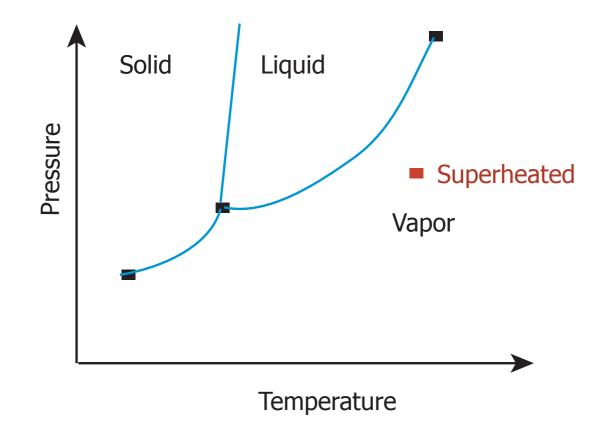


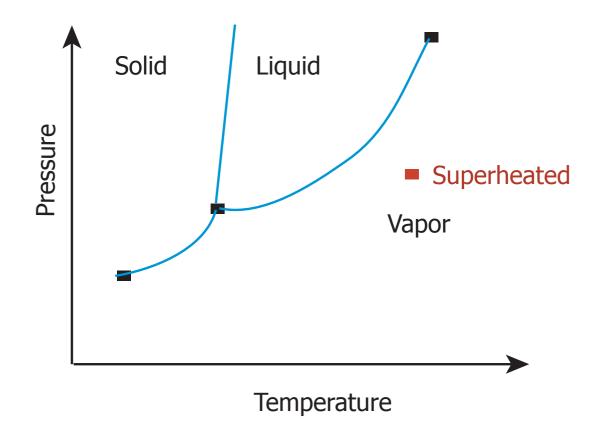
- At equilibrium, the pressure exerted by the vapor on the liquid is called the vapor pressure of the liquid.
- The value of the vapor pressure is independent of the amount of liquid in the container.
- Vapor pressure increases with temperature.
- The boiling point of a liquid is the temperature at which the vapor pressure equals the total pressure. At this point, liquid and vapor may co-exist in any proportion indefinitely.



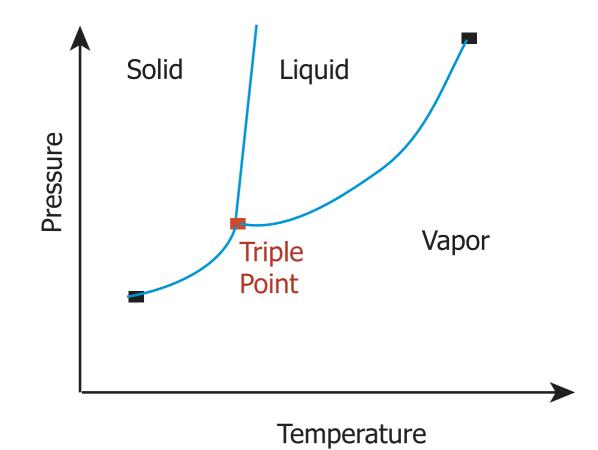


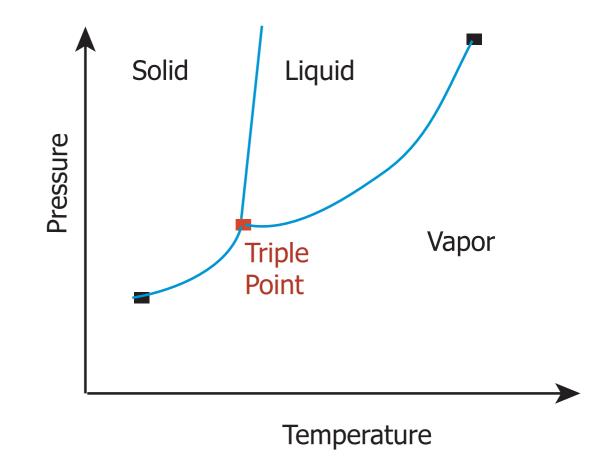
Liquid and vapor represented by points on the vapor pressure curve are called saturated liquid and saturated vapor respectively.



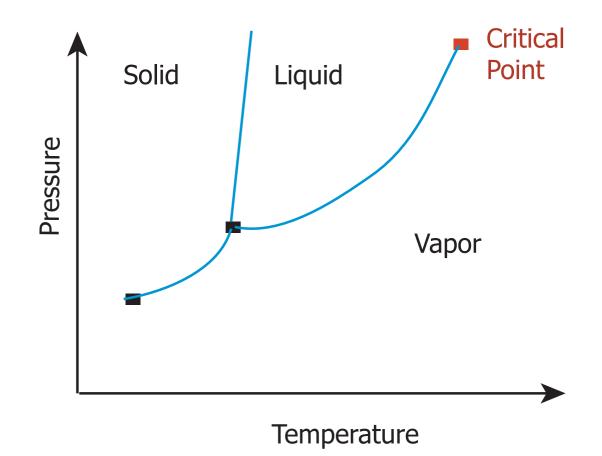


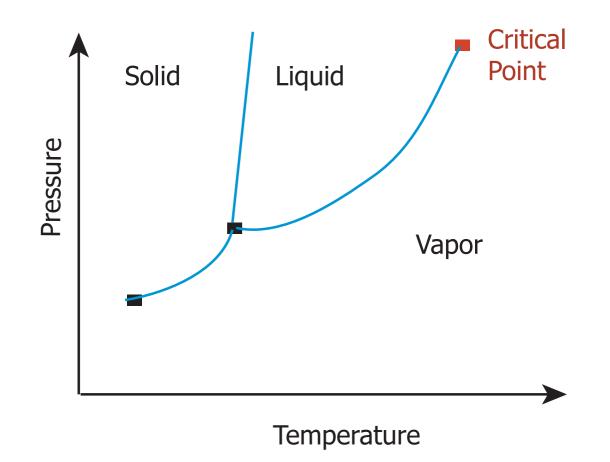
Vapor or gas at temperature above that corresponding to saturated is called superheated.



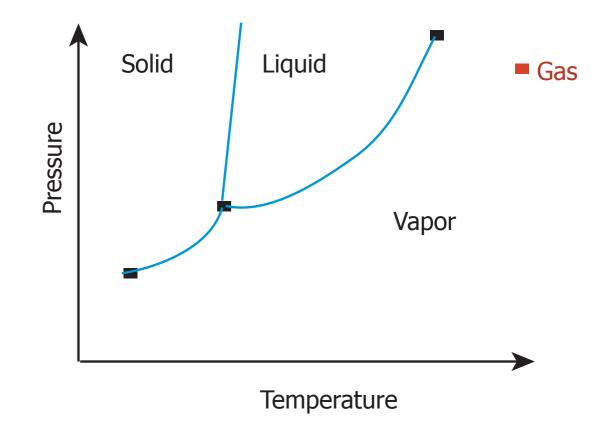


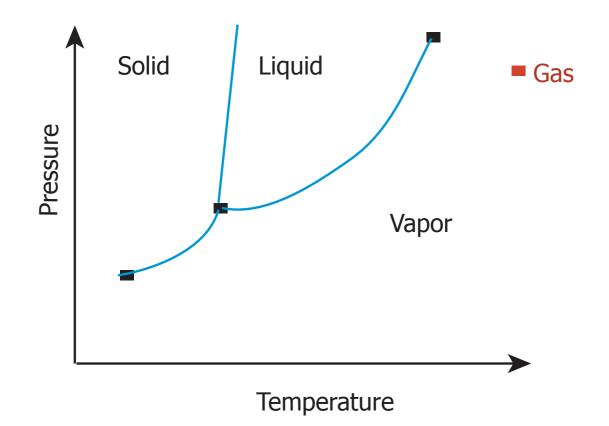
All three states co-exist at the triple point.





At the critical point, distinction between liquid and vapor disappears and all properties of the liquid, such as density, viscosity, refractive index etc. are identical to that of the vapor.





The substance at the temperature above the critical point is called a gas and it will not be liquified at this temperature regardless of how high the pressure might be imposed.

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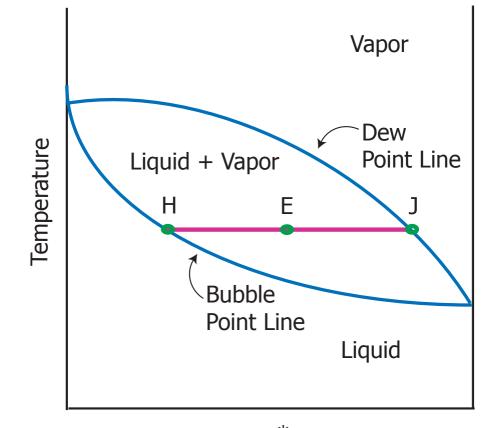
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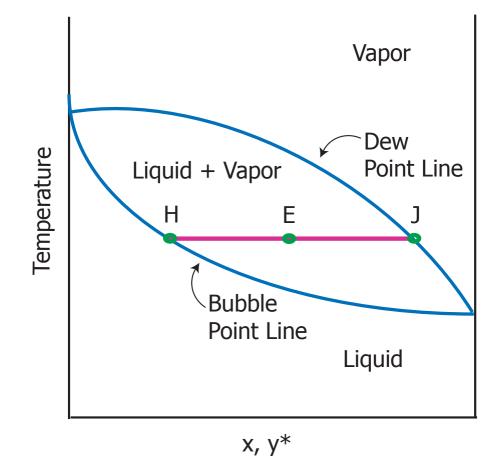
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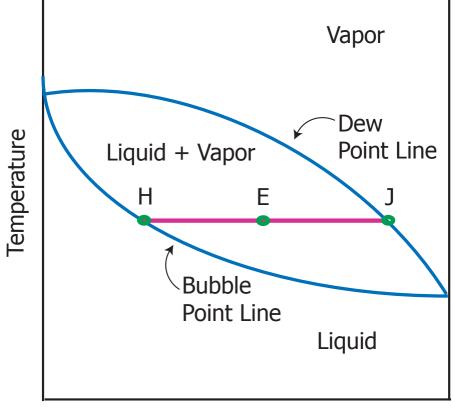
- Similar to pure substances, there will be a Pressure-Temperature relationship.
- However, there is an additional variable, concentration (usually represented by mole fraction)
  - x: mole fraction of A in liquid
  - y\*: corresponding mole fraction of A in vapor
  - (1-x): mole fraction of *B* in liquid
  - (1 y\*): corresponding mole fraction of A in vapor



• At point *H*, the mixture is a saturated liquid.

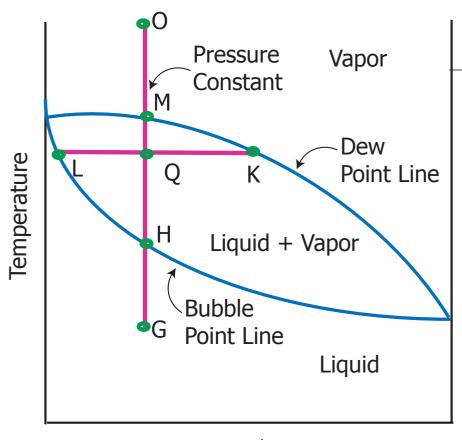


- At point H, the mixture is a saturated liquid.
- At point J, the mixture is a saturated vapor.



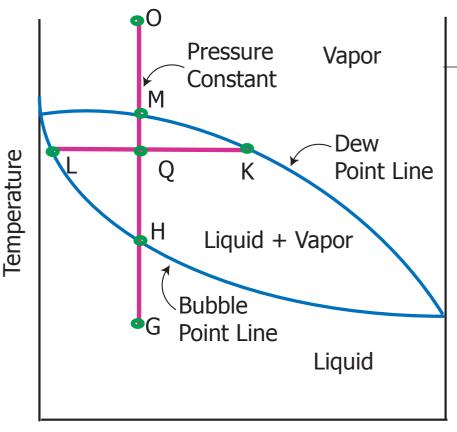
- At point H, the mixture is a saturated liquid.
- At point J, the mixture is a saturated vapor.
- At point E, the mixture is a two phase mixture with liquid phase composition of H and vapor phase composition of J such that the average composition of the entire mixture is E.

At point G, the mixture is a liquid.



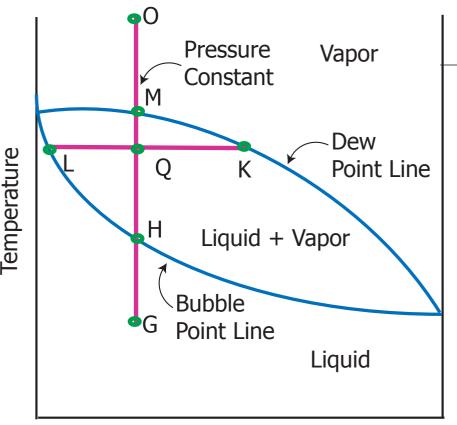
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- At point G, the mixture is a liquid.
- As temperature is raised, at point *H*, the mixture is a saturated liquid.



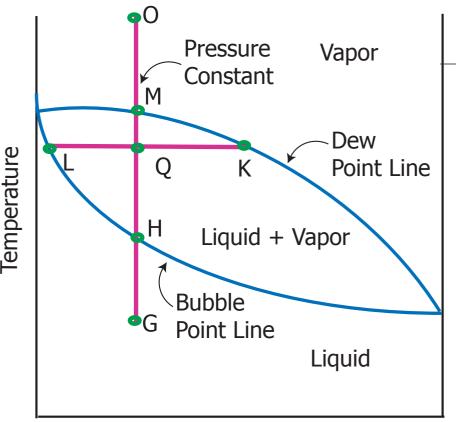
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- At point G, the mixture is a liquid.
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- At point Q, the mixture is a two phase mixture with liquid phase composition



of L and vapor phase composition of  $K^{x, y^*}$ 

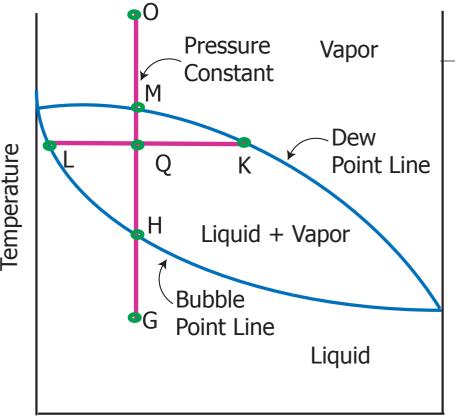
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At point M, the mixture is a saturated vapor.

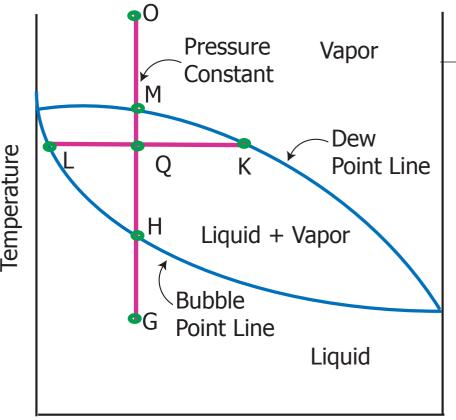
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- At point O, the vapor is superheated.

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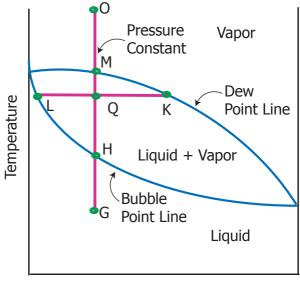
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Note that "boiling" occurs between H and M, and not at a constant temperature as in pure substances.

#### **Relative Volatility**

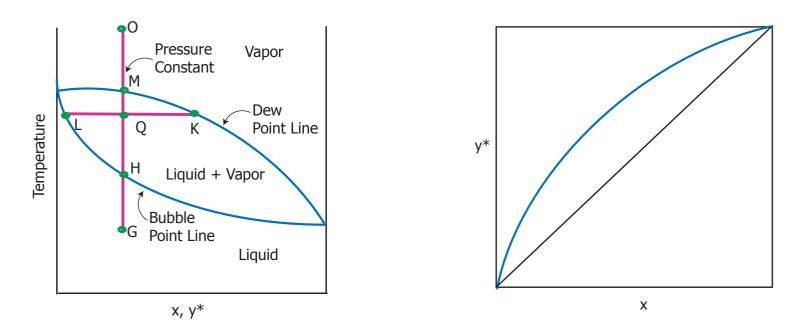
#### **Relative Volatility**



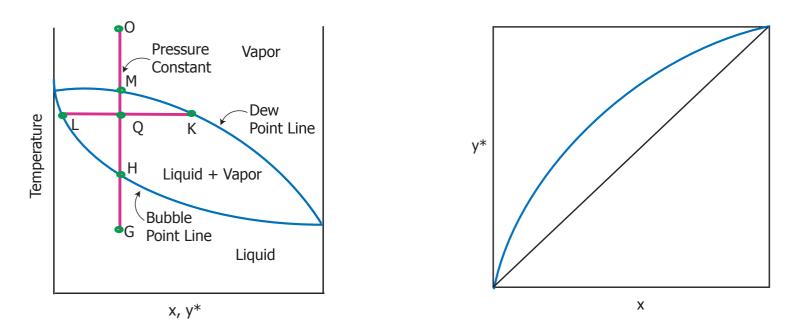
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#### If we plot $y^*$ vs. x at constant pressure,

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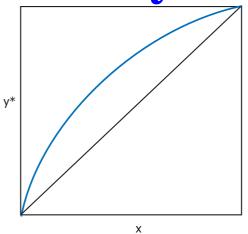
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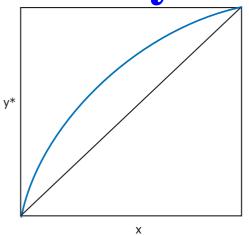
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A numerical measure of ease of separation is called relative volatility

Relative Volatility,  $\alpha$ , is the ratio of the concentration of *A* and *B* in one phase to that in the other.

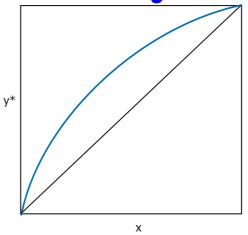


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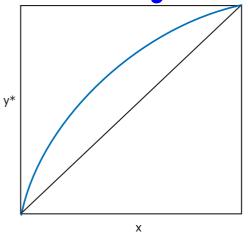
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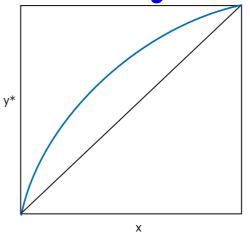
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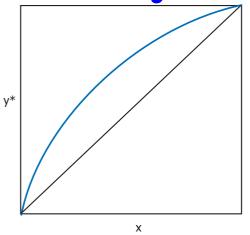
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If  $y^* = x$  (except at x = 0 or x = 1),  $\alpha = 1.0$  and no separation is possible. The larger the value of  $\alpha$  above unity, the easier it is to separate A and B.

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At a given pressure and temperature, one mole of any gas that is ideal will have exactly the same volume. One does not need to do experiments to determine this volume.

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Characteristics of Ideal Solutions:

- 1. The average intermolecular forces of attraction and repulsion in the solution are unchanged on mixing the constituents.
- 2. The volume of the solution varies linearly with composition.
- 3. The is neither absorption nor evolution of heat in mixing the constituents.
- 4. The total vapor pressure of the solution varies linearly with composition expressed as mole fraction.

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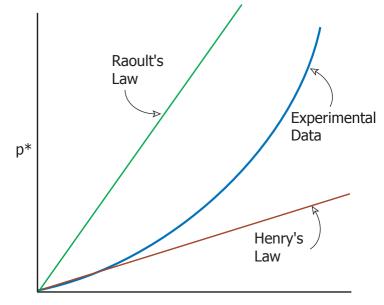
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- 2. Solubility of a particular gas in any solvent is the same.
- 3. If the gas behavior is non-ideal, the pressure can be replaced by fugacity.

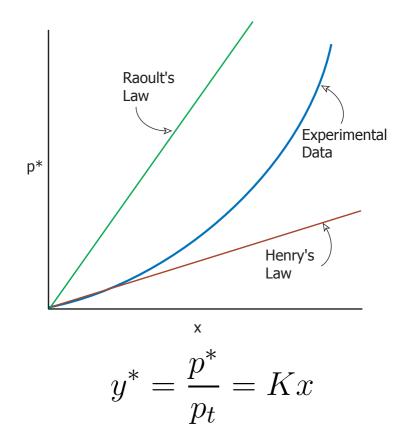
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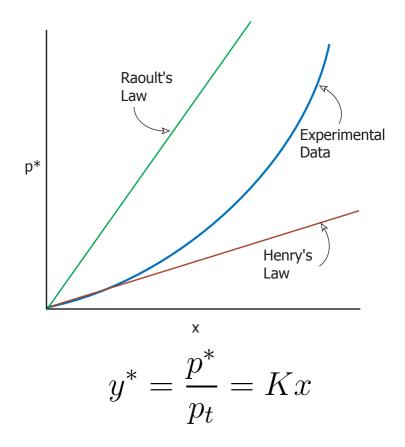


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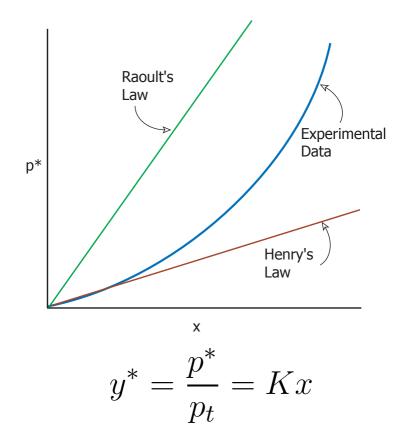


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Thus, while vapor pressures of A and B may vary considerably at different temperatures, their ratio will be constant provided the solution is ideal.

# Example

Compute the vapor-liquid equilibria of n-heptane (A) and n-octane (B) at 760 mm Hg given the following vapor pressure data:

$T (^{o}C)$	$p_A^0$ (mm Hg)	$p_B^0$ (mm Hg)
98.4	760	333
105.0	940	417
110.0	1050	484
115.0	1200	561
120.0	1350	650
125.6	1540	760

Verify that  $\alpha$  is nearly constant in the above temperature range.

#### **Solution Strategy**

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110.0	1050	484	0.487	0.674	2.17
115.0	1200	561	0.312	0.492	2.14
120.0	1350	650	0.157	0.279	2.08
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120.0	1350	650	0.157	0.279	2.08
125.6	1540	760	0.000	0.000	2.03

Although  $p_A^0$  and  $p_B^0$  vary considerably,  $\alpha$  is nearly constant. An average value of  $\alpha$  is 2.16.

$T (^{o}C)$	$p_A^0$ (mm Hg)	$p_B^0$ (mm Hg)	x	$y^*$	$\alpha$
98.4	760	333	1.000	1.000	2.28
105.0	940	417	0.655	0.810	2.25
110.0	1050	484	0.487	0.674	2.17
115.0	1200	561	0.312	0.492	2.14
120.0	1350	650	0.157	0.279	2.08
125.6	1540	760	0.000	0.000	2.03

Although  $p_A^0$  and  $p_B^0$  vary considerably,  $\alpha$  is nearly constant. An average value of  $\alpha$  is 2.16.

The equation 
$$\alpha = \frac{y^*(1-x)}{x(1-y^*)}$$
 can be rearranged to give:

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The equation  $\alpha = \frac{y^*(1-x)}{x(1-y^*)}$  can be rearranged to give:  $y^* = \frac{2.16x}{1+1.16x}$