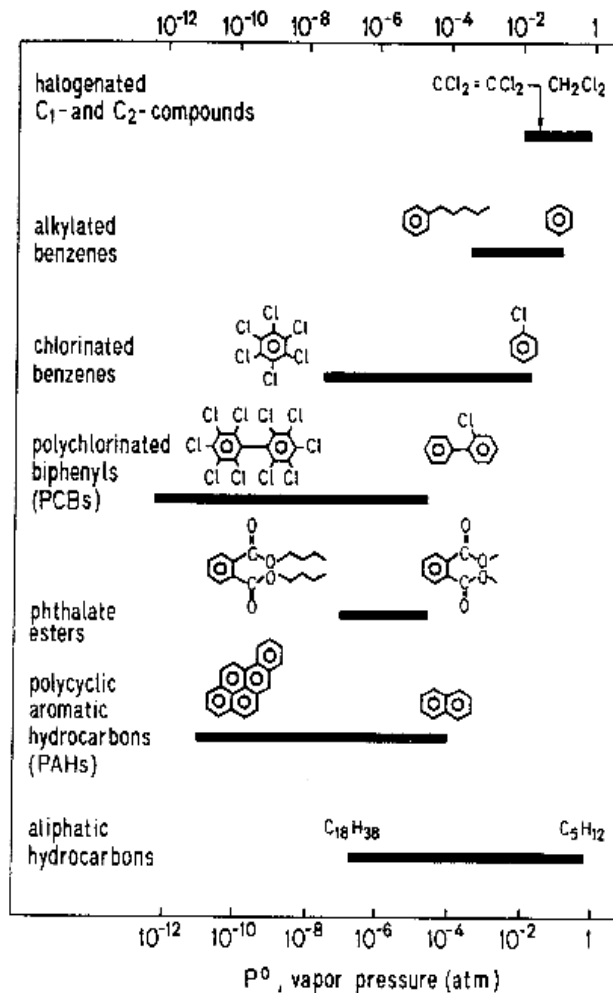


VAPOUR PRESSURE

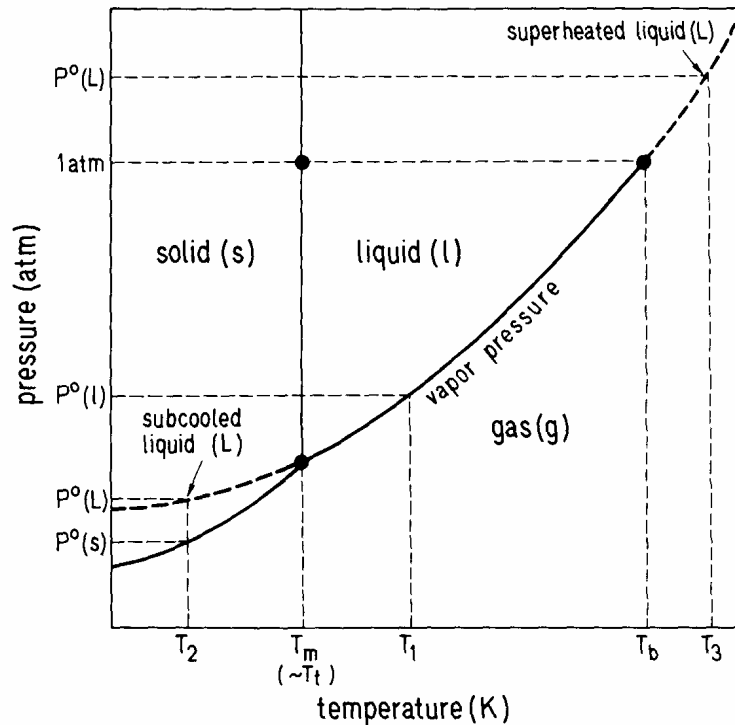
The vapor pressure (P°) is the pressure of the vapor of a compound in equilibrium with its pure condensed phase (solid or liquid). Vapour pressures depend strongly on the temperature and vary widely with different compounds due to differences in molecule – molecule interactions. The normal boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid is 1 atmosphere ($P^\circ = 1 \text{ atm}$). The vapour pressure of a substance is an intrinsic physical property that plays a crucial role in determining its distribution to and from gaseous environmental phases (the atmosphere, marsh bubble gas). The vapour pressure is also crucial for the prediction of equilibrium distribution coefficients to and from natural waters, such as Henry's Law constant (K_H).

Ranges of Vapour Pressures for some Important Classes of Organic Compounds at 25°C



Phase Diagrams

Simplified phase diagram of organic liquids and solids showing hypothetical subcooled and superheated liquid boundaries.



- Boiling point: temperature at which the liquids vapour pressure equals the external pressure.
- Normal boiling point: temperature at which the liquids vapour pressure equals 1 atm.
- Triple point: the temperature and pressure at which the solid, liquid and gas are at equilibrium.
- Vapourization curve: at any point on this line (specified by a temperature and pressure) the liquid and gas are at equilibrium.
- Fusion curve: at any point on this line (specified by a temperature and pressure) the solid and liquid are at equilibrium.
- Sublimation curve: at any point on this line (specified by a temperature and pressure) the solid and gas are at equilibrium.
- Critical point: at any point with a higher temperature and pressure than the critical temperature and pressure, the densities of the gas and liquid are equal. The gas and the liquid have become one phase described as a supercritical fluid.

Kinetic Molecular Theory:

At ambient temperatures, the vapor pressure of a compound can vary by an order of magnitude, so the dependence on temperature is important. It is illustrative to imagine what the molecules of a substance achieve to establish an equilibrium vapor pressure by examining a kinetic-molecular description. The molecules in the liquid will be thermally jostling each other and will be continuously exchanging energies. At a given temperature, the energies of the molecules in the liquid will have a distribution of energies according to the Maxwell-Boltzmann distribution. Some of these molecules will have sufficient energy to overcome the intermolecular forces of attraction. **Those molecules on the surface of the liquid with energies greater than the intermolecular forces** will escape the liquid. The concentration (partial pressure or vapor pressure) of the molecules above the liquid will steadily increase and the rate of collisions will also increase. A fraction of these colliding molecules will lose sufficient energy so that if they come in contact with the liquid surface, they will become trapped again. When the rate of escape (evaporation) from the liquid equals the rate of entrapment (condensation), the partial pressure of the gas above the pure liquid is called the equilibrium vapor pressure, P° .

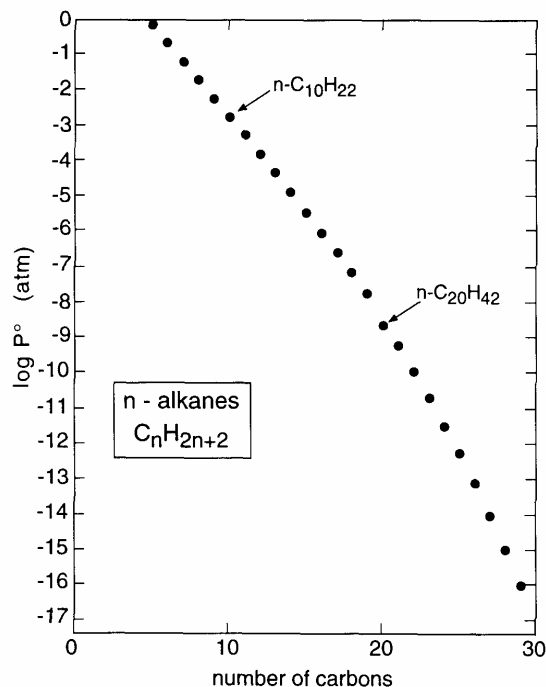
The fraction of molecules in the liquid with energy greater than the intermolecular forces is given by the Maxwell-Boltzmann distribution, $e^{-\text{energy}/RT}$, and the vapor pressure will be proportional to this term:

$$P^\circ \propto e^{-\text{energy}/RT}$$

and so

$$\ln P^\circ = -\frac{\text{energy}}{RT} + \text{constant}$$

Vapour pressure at 25°C of n-alkanes as a function of chain length.



Note: Larger n-alkane molecules have lower P° due to greater polarizability and hence increased strength of London Dispersion intermolecular forces.

Thermodynamics:

It can be shown that the temperature dependence of pressure is related to the change in molar enthalpy and the molar volume upon vapourization.

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V_{\text{vap}}}$$

For vaporization and sublimation, this equation may be simplified by assuming the vapor obeys the perfect gas law and by neglecting the molar volume of the liquid. Substituting RT/P for the change in molar volume yields;

$$\frac{dP^o}{dT} = \frac{P^o \Delta H_{\text{vap}}}{RT^2}$$

ΔH_{vap} (heat of vaporization) or ΔH_{sub} (heat of sublimation) is the enthalpy required to convert one mole of liquid or solid into a vapor. Assuming ΔH_{vap} is constant, integration yields:

$$\ln P^o = -\frac{\Delta H_{\text{vap}}}{RT} + \text{constant} \quad \text{for the vaporization of a liquid}$$

or

$$\ln P^o = -\frac{\Delta H_{\text{sub}}}{RT} + \text{constant} \quad \text{for the vaporization of a solid}$$

With the exception of a few classes of compounds (e.g., low molar mass hydrocarbons and some halogenated methanes such as freons), the majority of environmentally relevant organic chemicals have boiling points well above ambient temperatures and these compounds exist primarily as solids or liquids at ambient temperatures. Over the range of ambient temperatures, ΔH_{vap} can be assumed constant.

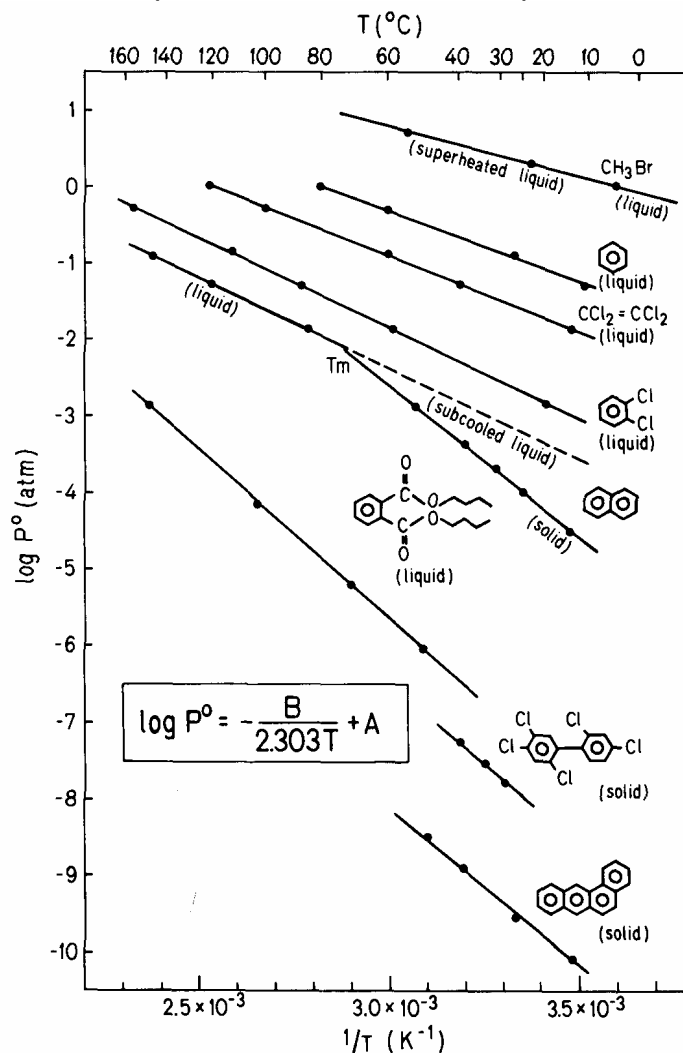
The figure below show the graphs of $\ln P^o$ versus $1/T$ for some representative compounds, note that the slopes are $-\Delta H/R$. The change in slope occurs at the phase transformation, liquid to solid and the ΔH term switches from ΔH_{vap} to ΔH_{sub} .

Another useful form of this equation, for the vapor pressures (P_1^o and P_2^o) above a liquid at temperatures T_1 and T_2 is:

$$\ln\left(\frac{P_2^o}{P_1^o}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ΔH_{sub} is substituted for ΔH_{vap} when considering the vapor pressure above a solid.

Temperature Dependence of Vapor Pressure for some Representative Compounds



If there is a phase change (liquid to solid) within the temperature range considered, the vapor pressure curve shows a break at this phase transition temperature (naphthalene in the figure above). Below the melting point, T_m the solid sublimates (solid \rightarrow gas), ΔH_{sub} can be considered to be:

$$\Delta H_{sub} = \Delta H_{vap}(L) + \Delta H_{melt}$$

In other words, the energy required to transform a solid to a gas is the sum of the energies to convert the solid to the liquid, ΔH_{melt} , plus the energy to convert the liquid to the gas, ΔH_{vap} . $\Delta H_{vap}(L)$ is the heat of vaporization of the hypothetical liquid at a temperature below the melting point, i.e., the imaginary liquid that is cooled below its melting point without allowing it to crystallize. This hypothetical state is commonly referred to as the *subcooled liquid state* and we will denote it with the symbol (L). This concept is important as we are using the pure liquid as our reference state for phase transfer processes and we represent the vapor pressure of the pure subcooled liquid as $P^\circ(L)$ and the vapor pressure of the pure solid as $P^\circ(s)$. The vapor pressure of the subcooled liquid can be obtained by extrapolation of vapor pressure data above the melting point (see naphthalene above).

At temperatures below the melting point we have:

$$\ln P^\circ(S) = -\frac{\Delta H_{sub}}{R} \left(\frac{1}{T} \right) + \text{constant} = -\frac{(\Delta H_{vap}(L) + \Delta H_{melt})}{R} \left(\frac{1}{T} \right) + \text{constant}$$

Vapour Pressure Estimation Methods

Empirical Approach:

Experimentally measured vapour pressures at different temperatures used to fit the Antoine Equation:

$$\ln P^{\circ} = -\frac{B}{T} + A$$

where T = temperature (Kelvin) and A & B are constants (pressure in atmospheres).

Plotting $\ln P^{\circ}$ vs $1/T$, with slope = B and intercept = A.

Values of A and B for many organic compounds are tabulated and available in CRC Handbook of Physics and Chemistry and a number of online resources. Use tabulated values for a given compound to calculate P° at any given temperature, T.

Semi-empirical Approach:

For non-hydrogen bonding molecules in liquid (or sub-cooled liquid) state, use;

$$\ln P^{\circ}(L) \cong 19 \left(1 - \frac{T_b}{T} \right) + 8.5 \left(\ln \frac{T_b}{T} \right)$$

Where T is the Kelvin temperature and T_b = normal boiling point (Kelvin), (pressure in atmospheres).

For non-hydrogen bonded molecules in solid state use;

$$\ln \frac{P^{\circ}(S)}{P^{\circ}(L)} \cong -[6.8 + 1.26(n - 5)] \left(\frac{T_m}{T} - 1 \right)$$

where T_m = normal melting point (Kelvin) and n = # flexing chain atoms and n = 5 for # flexing chain atoms < 5, (pressure in atmospheres).

Molecular Modeling Approach:

Input chemical structure → Molecular mechanics determine 3D geometry → Calculate surface area, dipole moments etc. → Estimate intermolecular forces → Predict physical properties (T_b , P° etc).