



UNIT-V IDEAL GASES AND REAL GASES

Joule Thomson Coefficient

The Joule–Thomson (Kelvin) coefficient

The rate of change of temperature T with respect to pressure P in a Joule–Thomson process (that is, at constant enthalpy H) is the Joule–Thomson (Kelvin) coefficient μ_{JT} . This is in terms of coefficient of the gas's volume V ,

can its heat capacity at constant pressure C_p , as

See the Appendix for the proof of this expressed in $^{\circ}\text{C}/\text{bar}$ (SI units: K/Pa) and depends on the type of gas and on the temperature and pressure of the gas before expansion.

All real gases have an inversion point at which the value of sign. The temperature of this point, the Joule–Thomson inversion temperature,

depends on the pressure of the gas before expansion. In a gas expansion the pressure decreases, so the sign of is always negative. With that in mind, the following table explains when the Joule–Thomson effect cools or warms a real gas:

Helium and hydrogen are two gases whose Joule–Thomson inversion temperatures

at a pressure of one atmosphere for are v helium). Thus, helium and hydrogen warm up when expanded at constant enthalpy

at typical room temperatures. On the other hand nitrogen and oxygen, the two most abundant gases in air, have inversion temperatures of 621 K (348 $^{\circ}\text{C}$) and 764 K (491 $^{\circ}\text{C}$) respectively: these gases can be cooled from room temperature by the Joule–Thomson effect.



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Derivation of the Joule–Thomson (Kelvin) coefficient

A derivation of the formula

for the Joule–Thomson (Kelvin) coefficient.

The partial derivative of T with respect to P at constant H can be computed by expressing the differential of the enthalpy dH in terms of dT and dP , and equating the resulting expression to zero and solving for the ratio of dT and dP . It follows from the fundamental thermodynamic relation that the differential of the enthalpy is given by:

$$dH = TdS + VdP$$

$$dH = C_p dT + \left[V + T \left(\frac{\partial S}{\partial P} \right)_T \right] dP$$

The remaining partial derivative of S can be expressed in terms of the coefficient of thermal expansion via a Maxwell relation as follows. From the fundamental thermodynamic relation, it follows that the differential of the Gibbs energy is given by:

$$dG = -SdT + VdP$$

The symmetry of partial derivatives of G with respect to T and P implies that:

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -V\alpha$$

where α is the coefficient of thermal expansion. Using this relation, the differential of H can be expressed as

$$dH = C_p dT + V(1 - T\alpha) dP$$



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