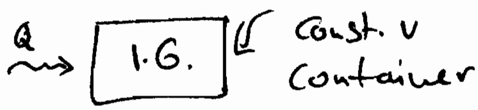
Ideal Gases

All gases at low pressures (no interactions between molecules, no quantum effects) approach this "ideal gas" state:

$$\boxed{\begin{aligned} PV &= NRT \\ P\underline{V} &= RT \end{aligned}} \qquad R = 8.314\ \frac{\text{J}}{\text{mol K}}$$

Since molecules are isolated, $U^{IG} = N\underline{U}^{IG}(T)$

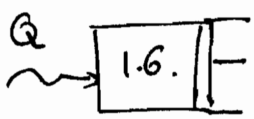
Define heat capacity (at const. V): $C_V^{IG} = \dfrac{d\underline{U}^{IG}}{dT}$



$\text{đ}Q = dU = NC_V^{IG}\,dT$

In general, C_V depends on density, $C_V \equiv \left(\dfrac{\partial \underline{U}}{\partial T}\right)_{\underline{V}}$

At const. P,



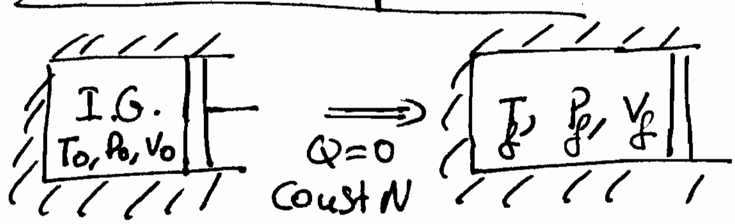
$$dU = \text{đ}Q - PdV = NC_P^{IG}\,dT \Rightarrow$$

$$d(U+PV) = dH = \text{đ}Q = NC_P^{IG}\,dT$$

$$C_P^{IG} = \frac{d\underline{H}^{IG}}{dT} = \underbrace{C_V^{IG} + R}_{\underline{H}^{IG} = \underline{U}^{IG} + P\underline{V} = \underline{U}^{IG} + RT}$$

In general, $C_P \equiv \left(\partial \underline{H}/\partial T\right)_P$

Adiabatic expansion



$dU = \cancel{\text{đ}Q} + dW =$

$= -PdV$

$V = \dfrac{NRT}{P}$

$$\left.\begin{aligned} du &= NC_v dT \\ dV &= \frac{NR}{P} dT - \frac{NRT}{P^2} dP \end{aligned}\right\} \Rightarrow C_v dT = -R dT + \frac{RT}{P} dP$$

$$\Rightarrow (C_v + R) dT = RT \frac{dP}{P} \Rightarrow \frac{C_P}{T} dT = R \frac{dP}{P} \Rightarrow$$

$$\Rightarrow C_P \ln T \Big|_{T_0}^{T_f} = R \ln P \Big|_{P_0}^{P_f} \Rightarrow \boxed{\left(\frac{T_f}{T_0}\right)^{C_P} = \left(\frac{P_f}{P_0}\right)^{R}}$$

Setting $C_P/C_v = \gamma \Rightarrow R/C_p = (\gamma-1)/\gamma$, $R/C_v = \gamma - 1$

$$T_f/T_0 = \left(P_f/P_0\right)^{\frac{\gamma-1}{\gamma}}$$

In a similar way, eliminating dP we get

$$T_f/T_0 = \left(V_f/V_0\right)^{1-\gamma} = \left(\underline{V}_f/\underline{V}_0\right)^{1-\gamma}$$

and eliminating dV

$$P_f/P_0 = \left(V_f/V_0\right)^{-\gamma} \Rightarrow P_f V_f^{\gamma} = P_0 V_0^{\gamma}$$

$$\text{or } \boxed{P V^{\gamma} = \text{const.}}$$

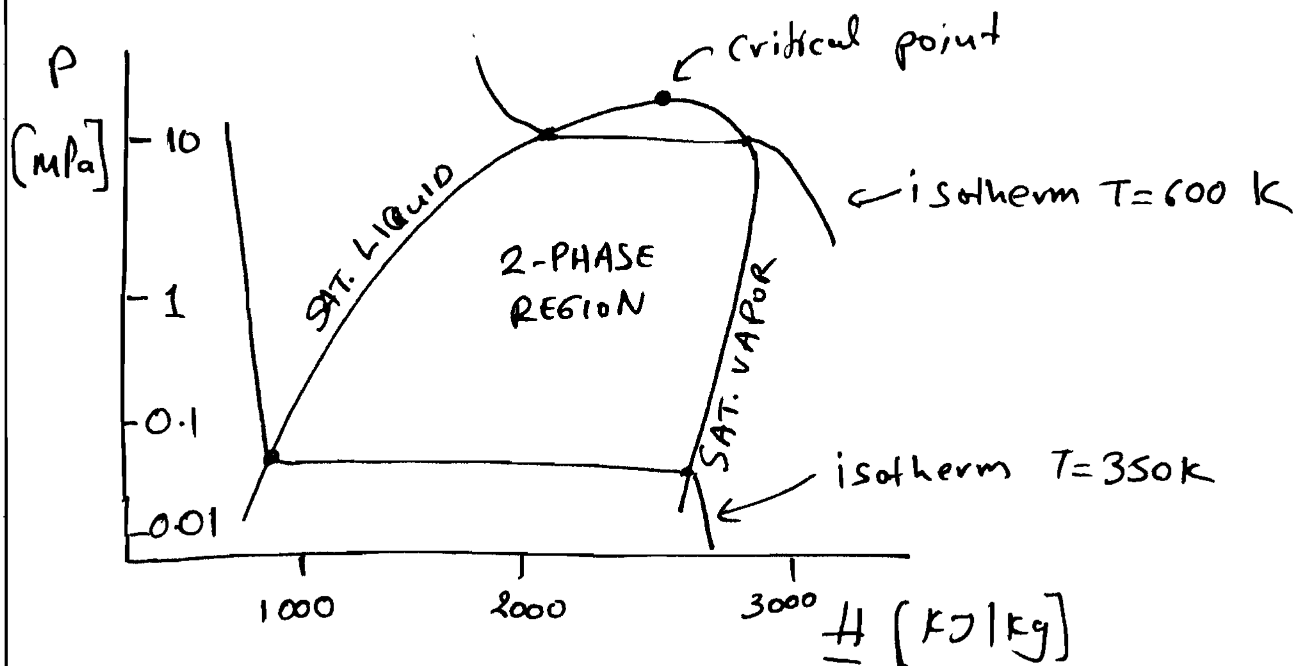
Real Fluids

Real substances deviate from ideal-gas behavior at moderate pressures ($\sim$ a few bar) and can exist as liquids or solids (phase transitions).

Thermodynamic properties such as $\underline{U}$ or $\underline{H}$ can be determined from experimental data (as described later, in Ch. 7).

Only differences in $\underline{U}$ or $\underline{H}$ between states are meaningful, so thermodynamic tables or diagrams rely upon a reference state at which $\underline{U}$ (or $\underline{H}$) are considered to be zero.

Eg. P-$\underline{H}$ (Mollier) diagram for steam:

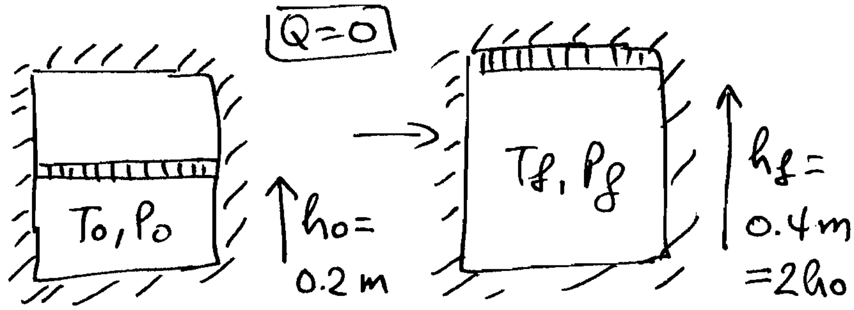


Primary data source (see App. I)

NIST Chemistry WebBook: webbook.nist.gov

* Equation-of-state ($P\underline{V}T$) + "derived" thermodynamic properties for ~70 pure components
* Thermochemical (reaction) data for many more

Example 2.13 Expansion of gas (CO_2)



area $A = 0.1\ m^2$
$P_0 = 2$ MPa
$T_0 = 300$ K
$m = 40$ kg
$g = 9.81\ m/s^2$

$T_f = ?$ (a) Assuming CO_2 is ideal, $C_v^{IG} = 28.91 \frac{J}{mol\,K}$

$$\Delta U = W \Rightarrow -mg(h_f - h_0) = N C_v \Delta T$$

$$N = \frac{PV}{RT} = \frac{P_0 A h_0}{R T_0} = 16.04 \text{ mol}$$

$$\boxed{T_f = 299.83\text{ K}}$$

$$P_f = P_0 \frac{V_i}{V_f}\frac{T_f}{T_0} = 2\text{ MPa}\ \frac{1}{2}\ \frac{299.83}{300} \Rightarrow \boxed{P_f = 0.9994\text{ MPa}}$$

(b) Using accurate data for CO_2 [NIST webBook]
→ Justified because 2 MPa is not that low!

$\rho_0(2\text{MPa}, 300\text{ K}) = 895.71 \frac{mol}{m^3}$, $N_0 = h_0 A \rho_0 = 17.91$ mol
[10% diff]

$\underline{U}_0 = 19.26$ kJ/mol ; $\Delta U = mg\Delta h = -78.5$ J

$$\rho_f = \rho_0/2 = 447.9 \frac{mol}{m^3}$$

$$U_f = U_0 - mg\Delta h = (17.91 \cdot 19.26 - 0.08)\text{ kJ}$$

$$\underline{U}_f = \frac{U_f}{N} = 19.26 \frac{kJ}{mol}$$

Isochoric calculation at $\rho_f, \underline{U}_f$ =>

$$\boxed{T_f = 289.6\text{ K} \qquad P_f = 1.016\text{ MPa}}$$

T_f is quite diff.
P_f is similar to I.G.