Thermodynamics lecture 10. Real gases and flow processes

1. Real (i.e. non-ideal) gases, critical point, critical parameters
2. The law of corresponding states
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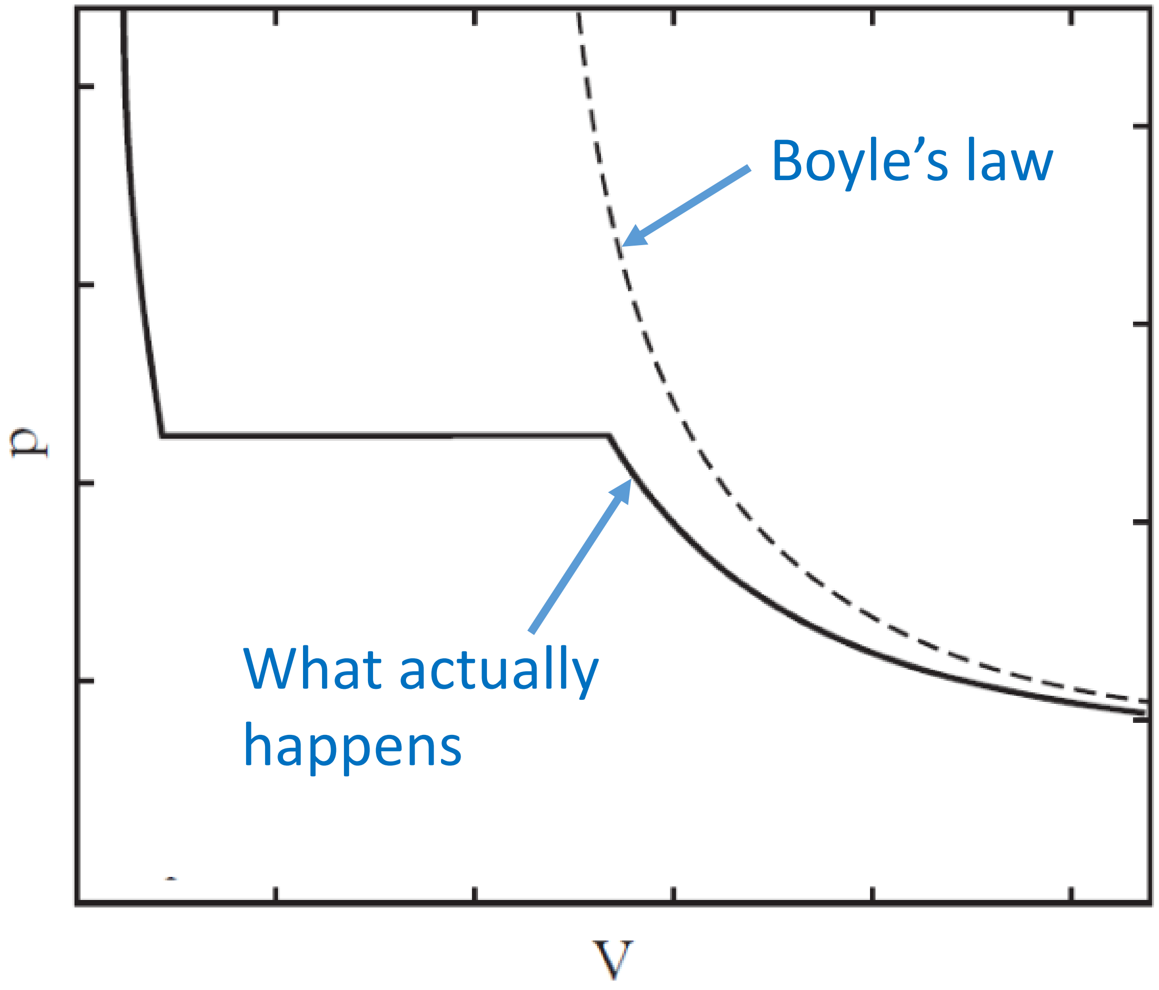
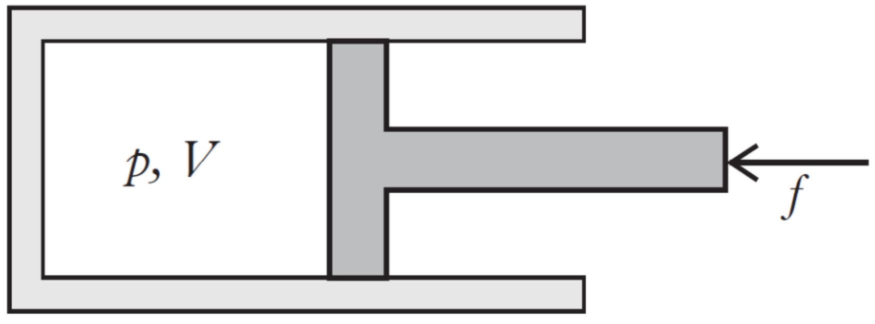
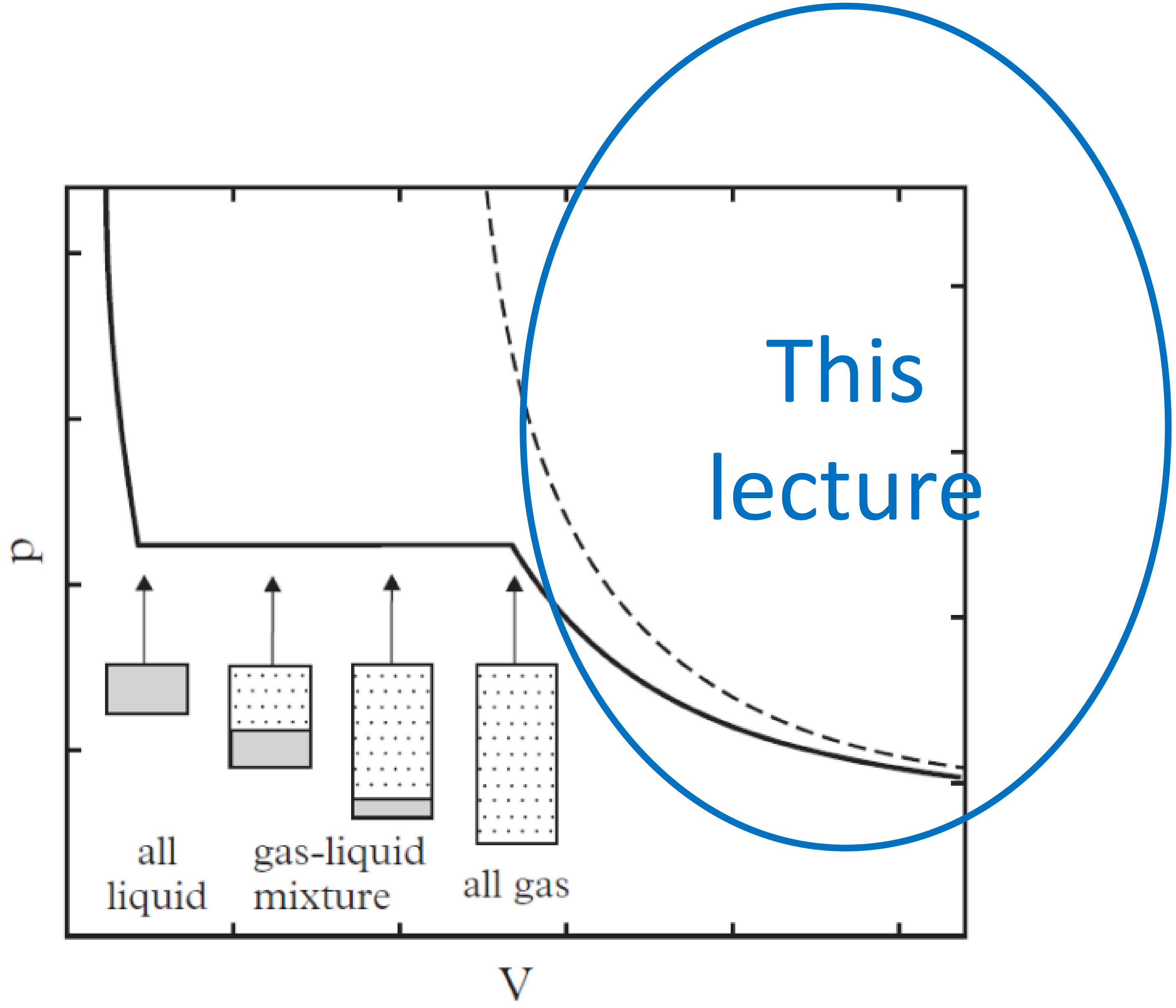
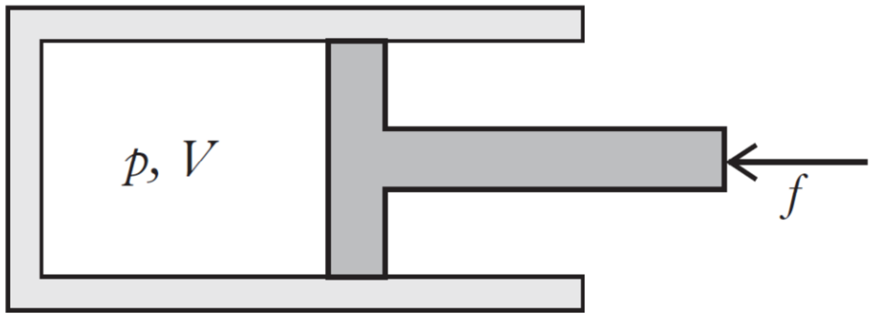
Compressing an ordinary substance at constant temperature






This
lecture
p
V
all
liquid
gas-liquid
mixture
all gas


p, V
f

van der Waals' equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

Redlich–Kwong equation

$$\left(p + \frac{a}{V_m(V_m + b)T^{1/2}}\right)(V_m - b) = RT.$$

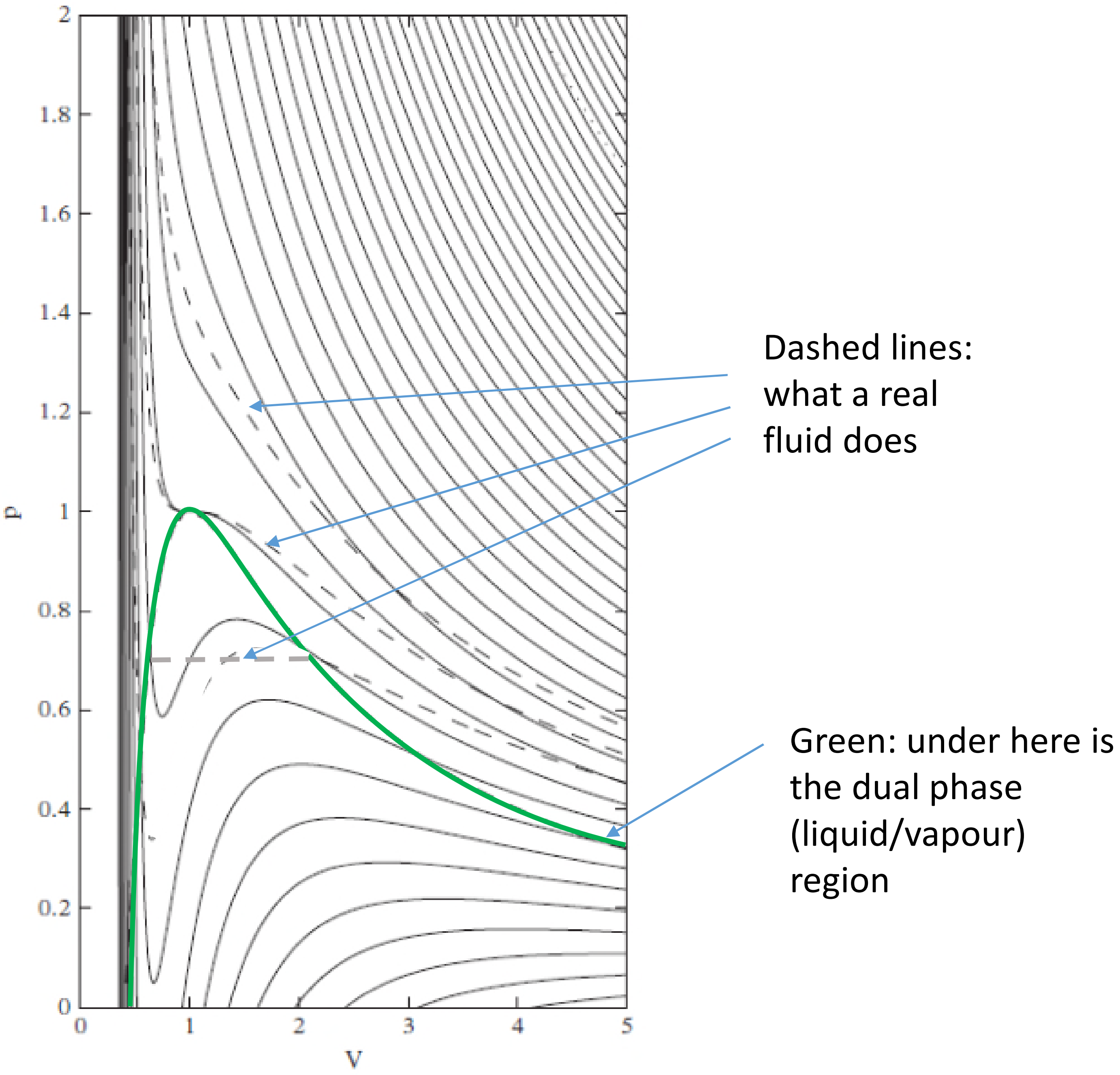
Dieterici's equation

$$p(V_m - b)\,e^{a/(RTV_m)} = RT.$$

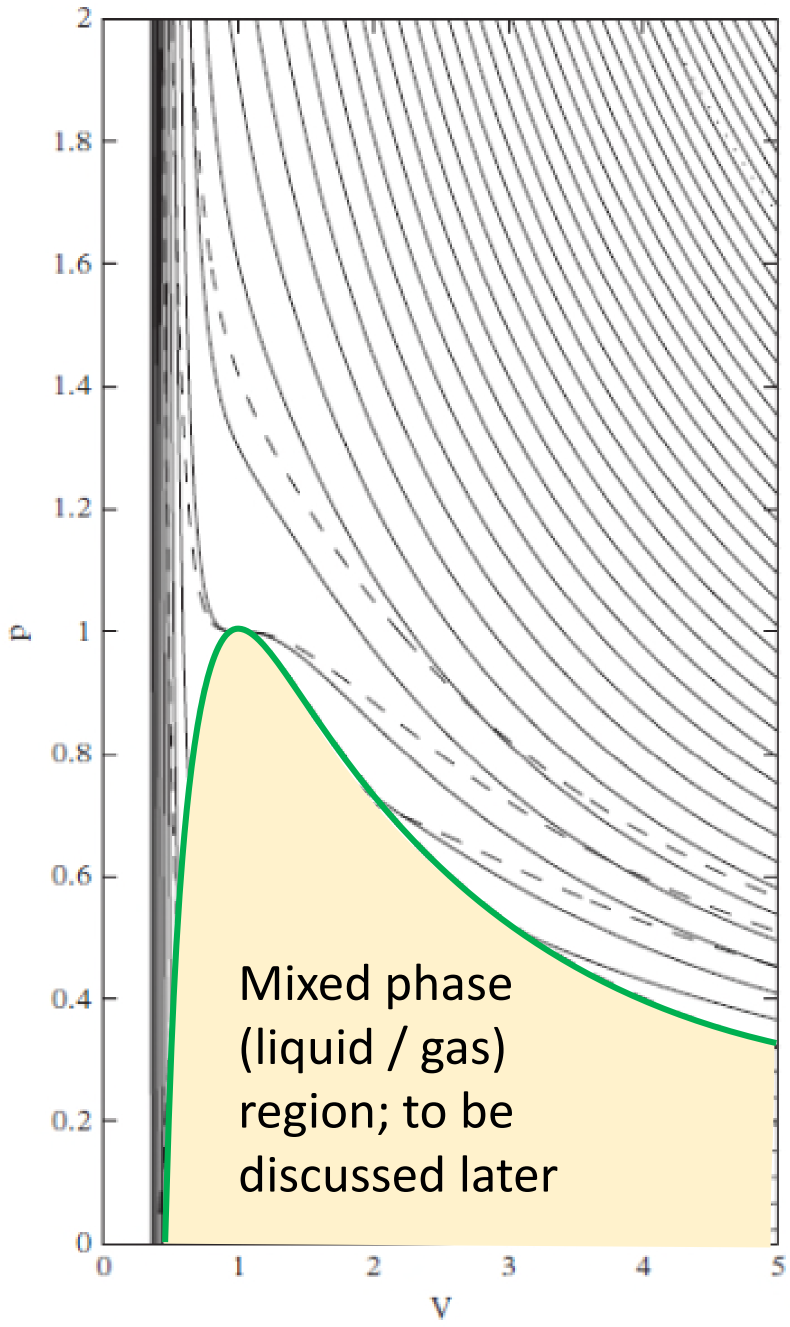
Virial expansion

$$PV_m = RT\left(1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \frac{B_4}{V_m^3} + \ldots\right)$$

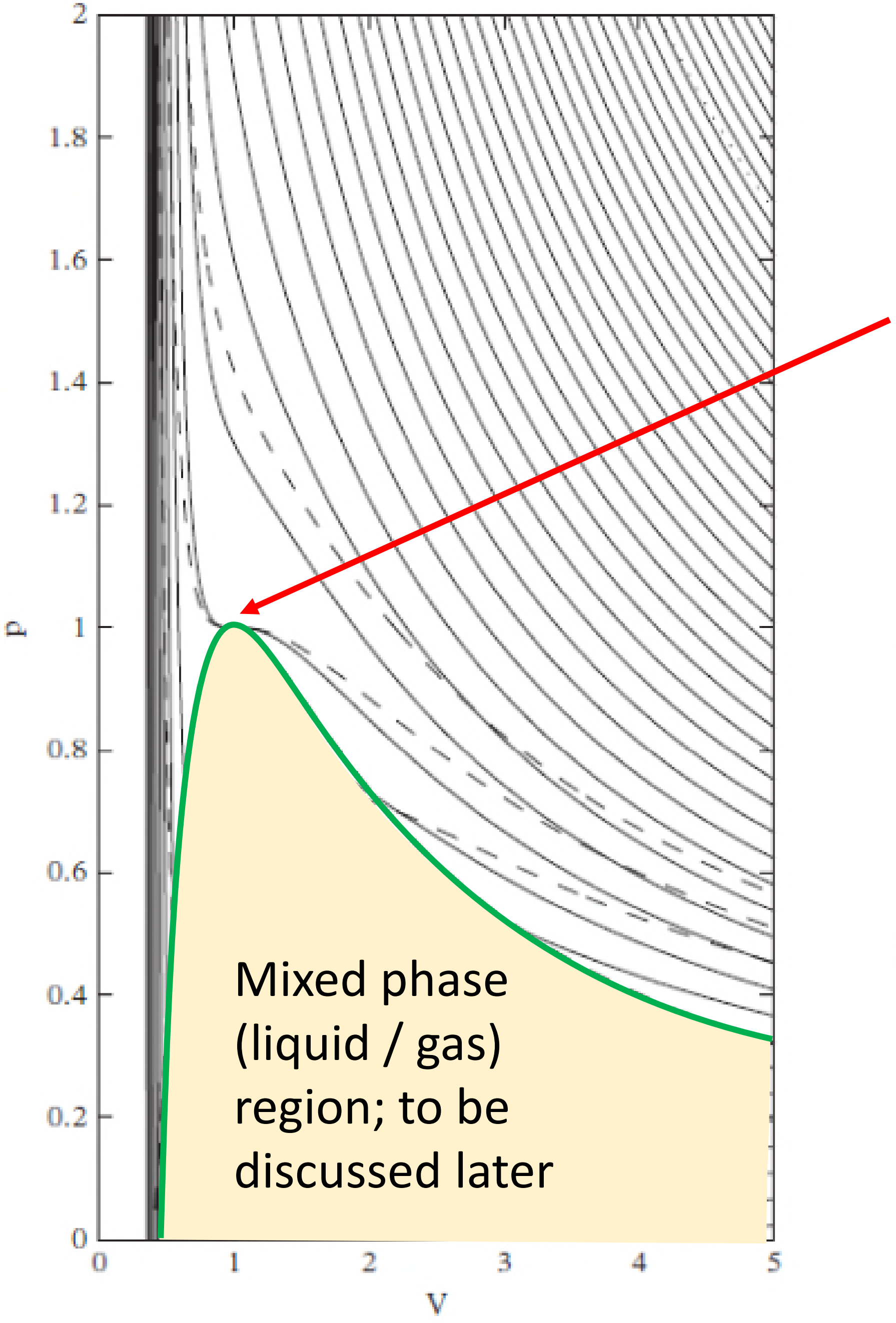
Isotherms predicted by van der Waals equation



Isotherms predicted by van der Waals equation



Isotherms predicted by van der Waals equation



Critical point:

Isotherm has a stationary point:

$$(\partial p/\partial V)_T = 0$$

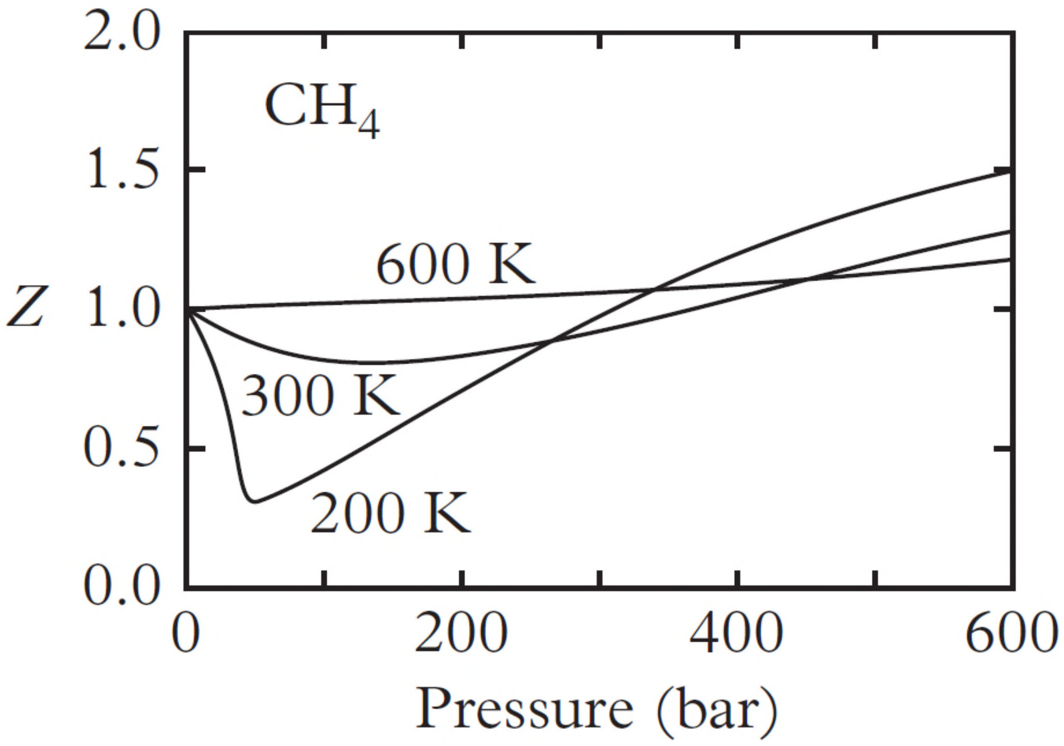
which is also a point of inflexion:

$$(\partial^2 p/\partial V^2)_T = 0$$

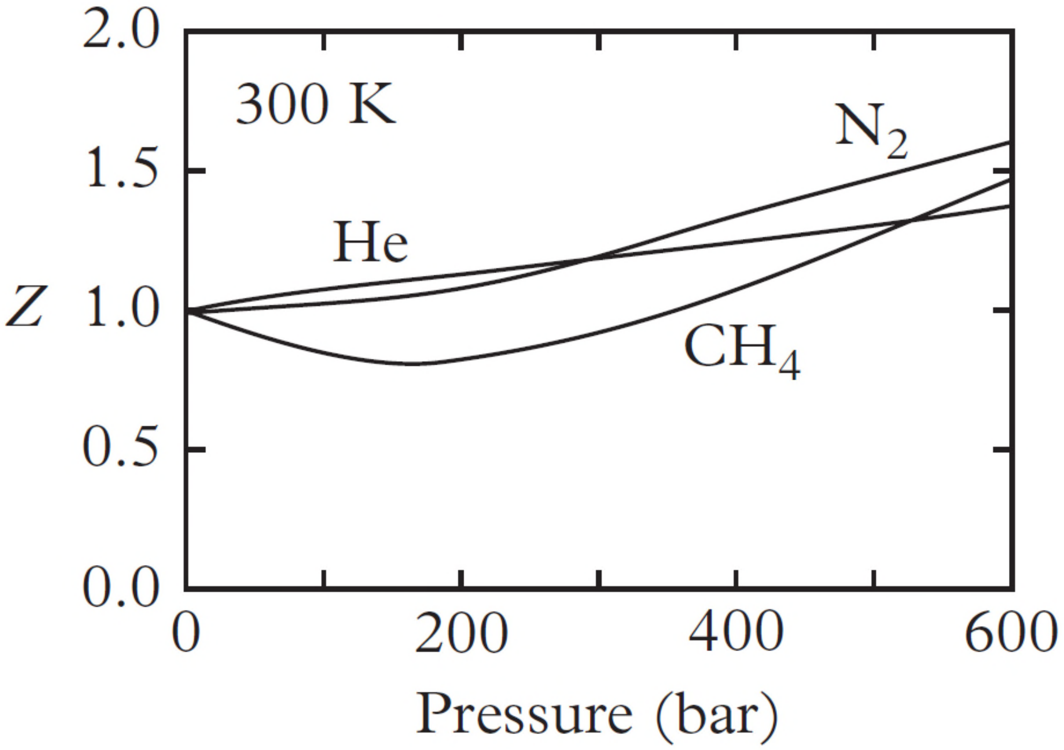
	Critical point			van der Waals parameters	
Gas	T_c (K)	p_c (MPa)	Z_c	a (J m^3 mol^{-2})	b (cm^3 mol^{-1})
Ne	44.4	2.76	0.311	0.0208	16.72
Ar	150.9	4.87	0.291	0.1363	32.19
Kr	209.4	5.50	0.288	0.233	39.57
Xe	289.7	5.84	0.287	0.419	51.56
N_2	126.2	3.39	0.289	0.1370	38.69
CH_4	190.6	4.60	0.286	0.230	43.06
CO_2	304.1	7.38	0.274	0.365	42.67
H_2O	647.1	22.06	0.229	0.5536	30.49
H_2	33.2	1.297	0.306	0.0248	26.60
He	5.19	0.227	0.301	0.00346	23.76

Compression factor (a way of saying how non-ideal the gas is)

$$Z = pV/RT$$



Methane at some example temperatures

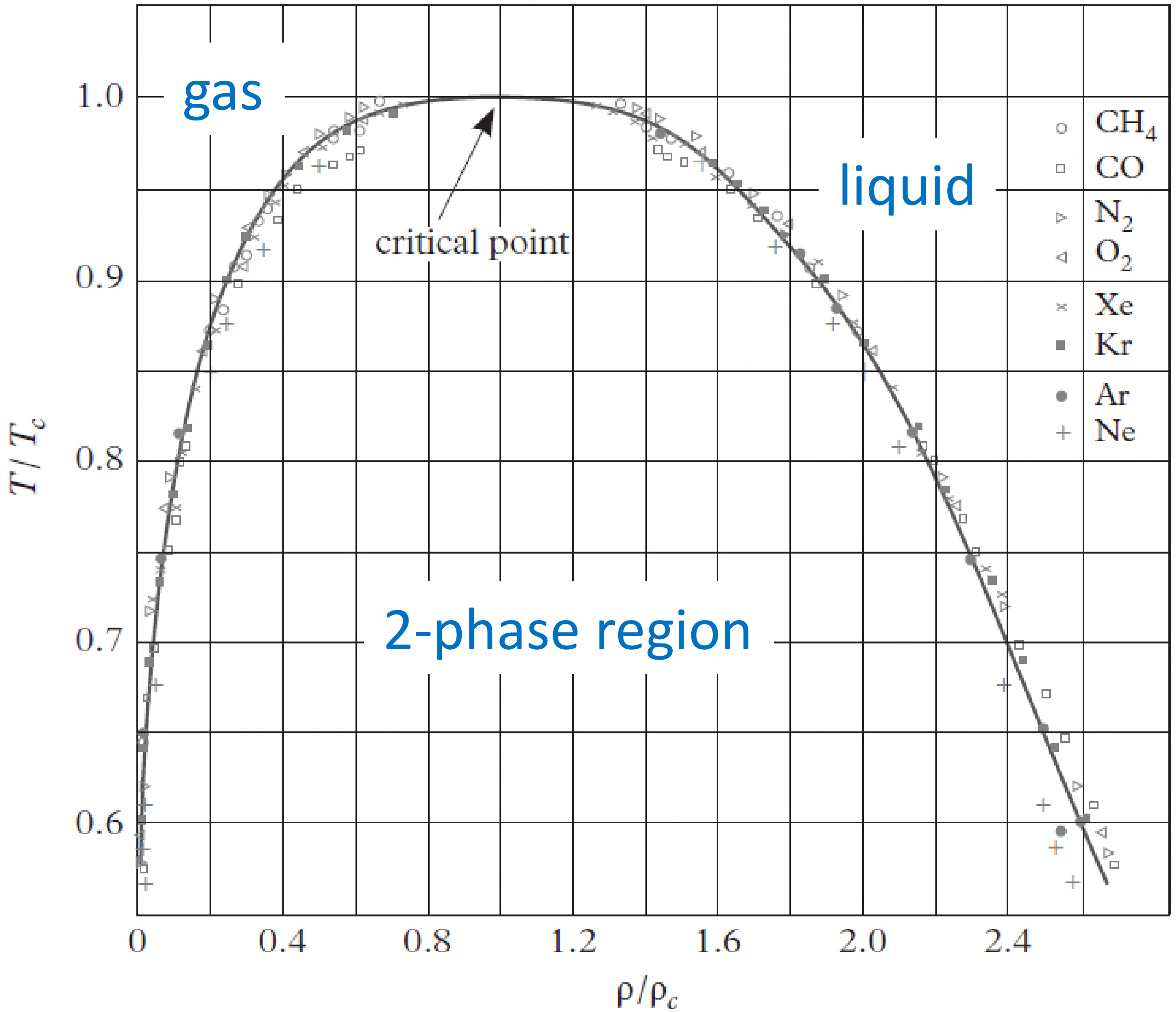


Some example gases at 300 K

Experimental evidence of the law of corresponding states

Plot the temperature vs density at the liquid/gas phase transition

Temperature, in units of critical temperature

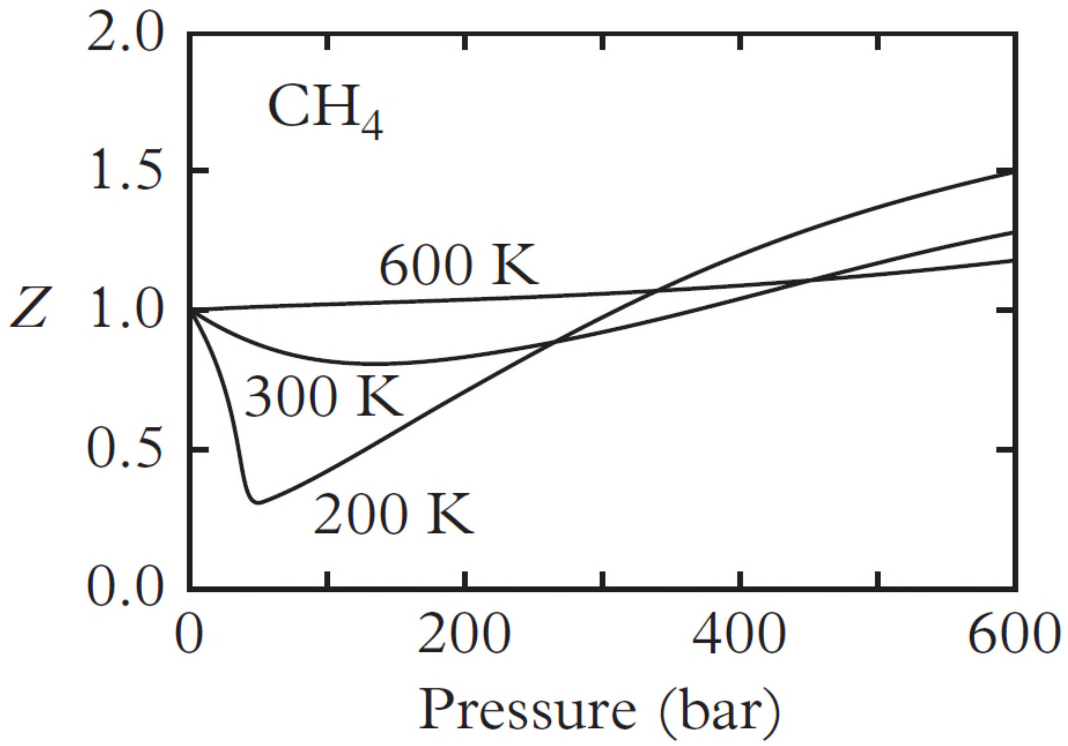


Density in units of critical density

(Adapted from Guggenheim (1945))

Compression factor (a way of saying how non-ideal the gas is)

$$Z = pV/RT$$



~~Methane~~ at some example temperatures

Any gas

(in suitably scaled units)

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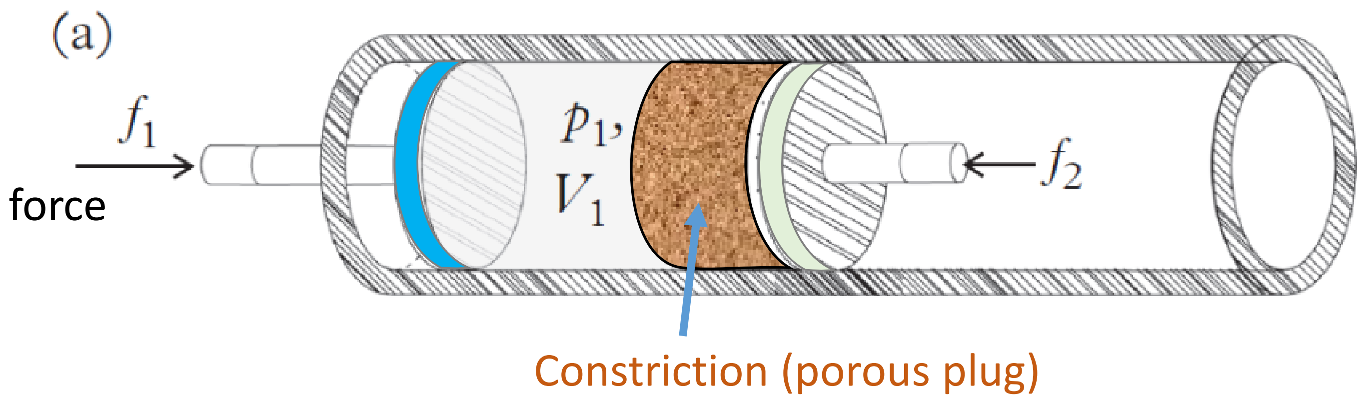
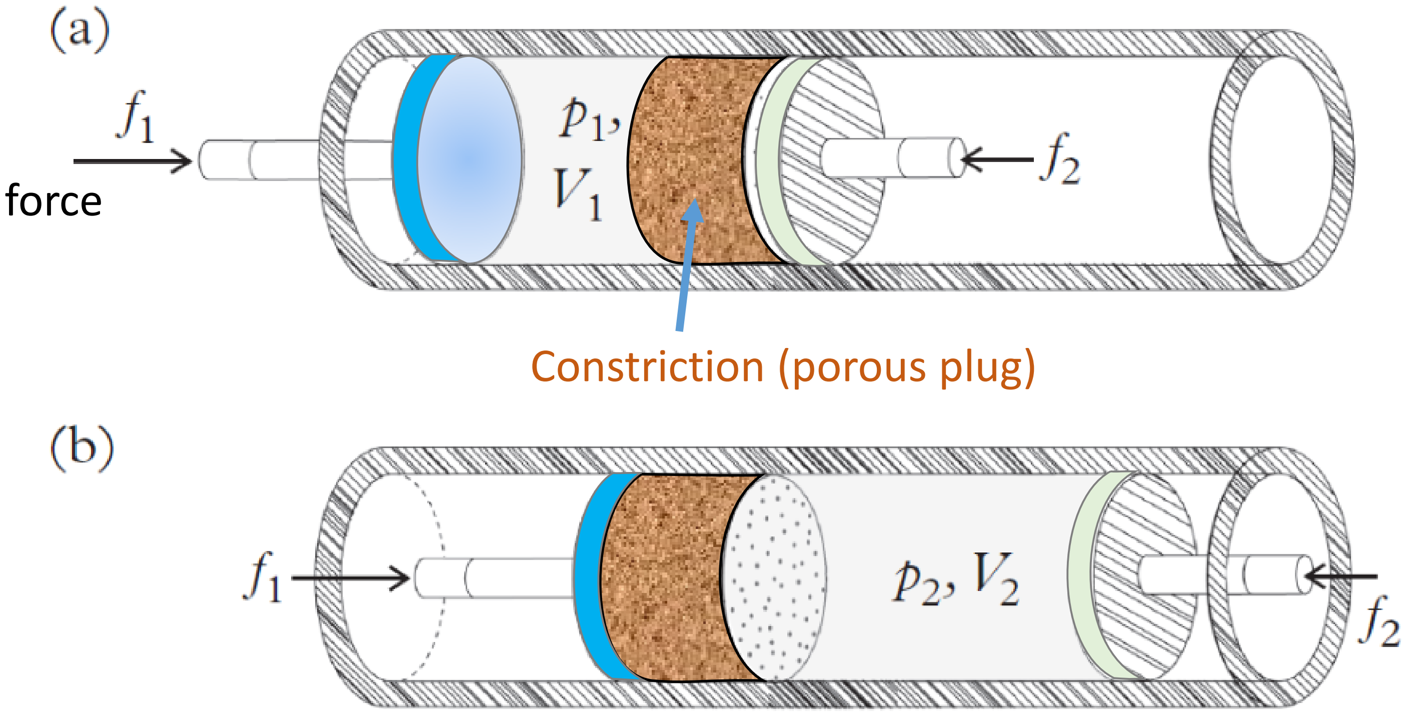
Joule-Kelvin process (also called throttle process)



- Thermal isolation
- Slow but non-zero rate of flow through a constriction (e.g. porous plug or small nozzle)

→ $f_1 > f_2$

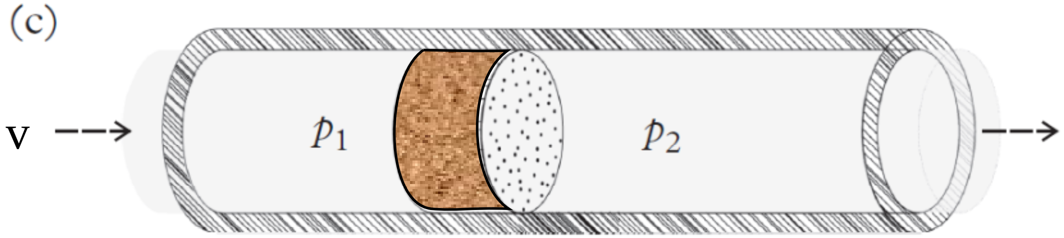
Joule-Kelvin process (also called throttle process)



- Thermal isolation
- Slow but non-zero rate of flow through a constriction (e.g. porous plug or small nozzle)

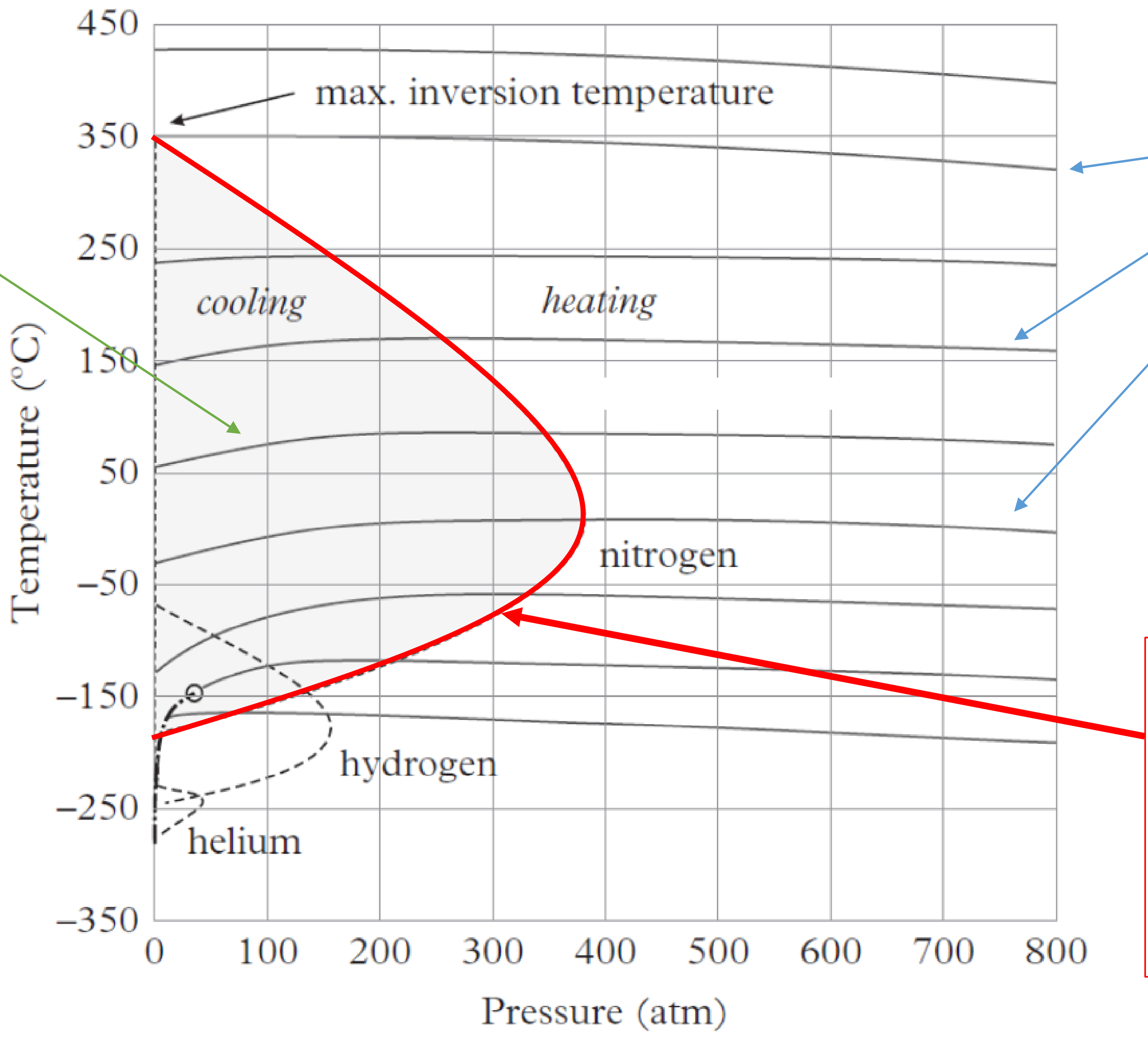
→ $f_1 > f_2$

f_1 and f_2 are maintained constant, therefore so are p_1 and p_2



Often done in practice in a continuous flow

Get **cooling** when $dT/dp > 0$ (think: pressure falls and we want T to fall)



Curves of constant enthalpy *(isenthalps)*

Inversion curve: where

$$\left.\frac{\partial T}{\partial p}\right|_H = 0$$

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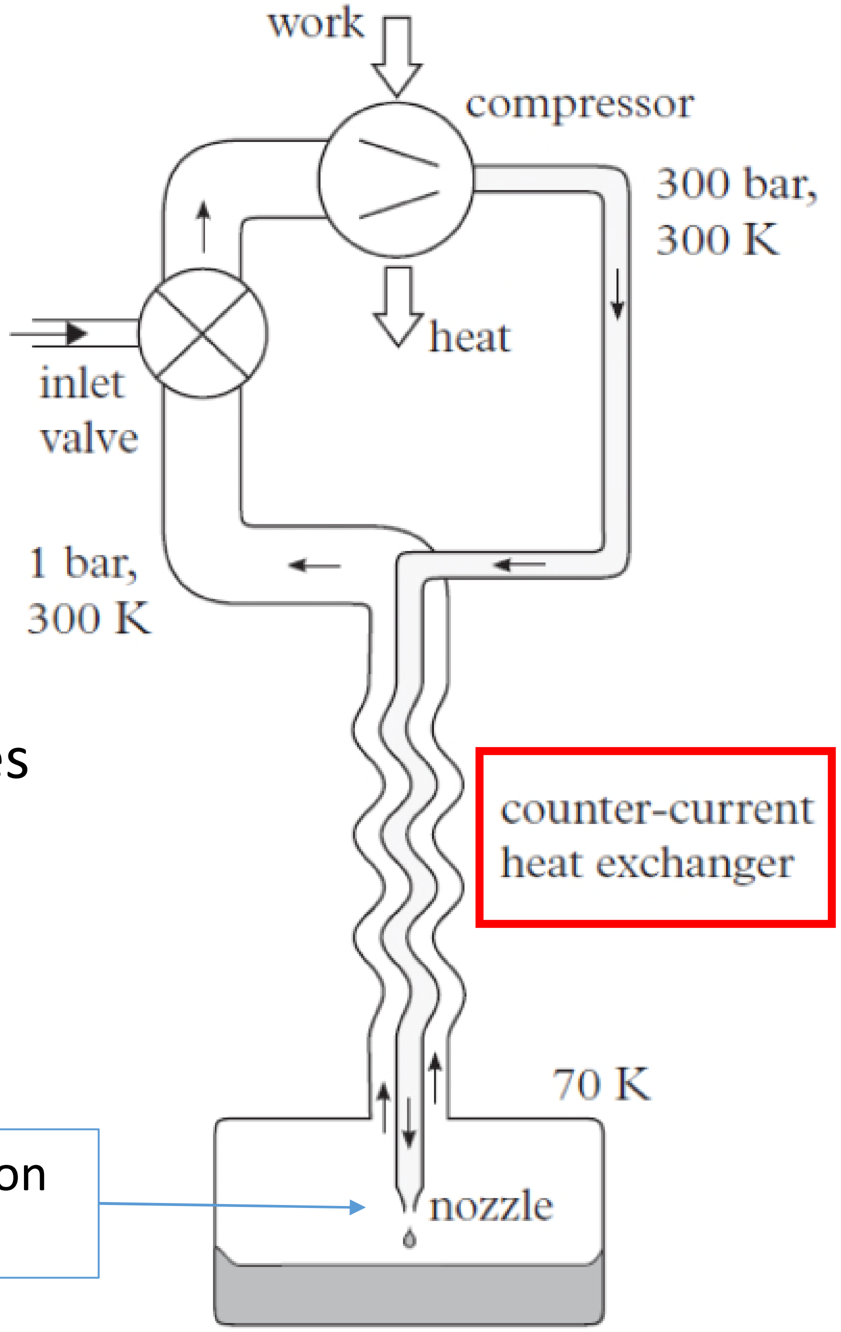
Linde process for liquefaction of gases



Example values for nitrogen

Joule-Kelvin expansion happens here

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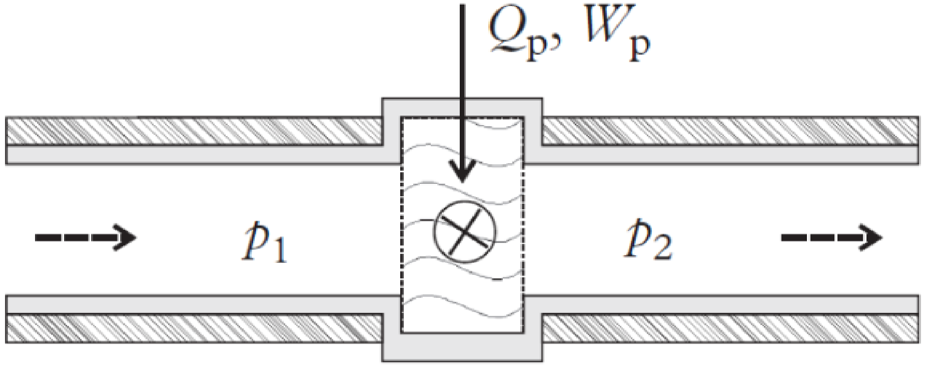
More general *flow process* (gas turbines, chemical process plants, etc.)

Process heat, process work



Conservation of energy:

$$Q_p + W_p = H_{out} - H_{in} \equiv \Delta H$$

e.g. adiabatic compressor:

$Q_p = 0, \qquad pV^\gamma = \text{const}$

→ work required to compress a given amount of flowing fluid:

$$W_p = \Delta H = \int V \mathrm{d}p$$

$$= V_1 \int_{p_1}^{p_2} \left(\frac{p_1}{p}\right)^{1/\gamma} \mathrm{d}p = \frac{\gamma V_1 p_1}{\gamma - 1}\left[\left(\frac{p_2}{p_1}\right)^{1-1/\gamma} - 1\right]$$