Lecture 27. *Cooling Real Gas*

- In this lecture, we will move beyond the ideal gas description and revisit fundamental aspects like Joule expansion
- We will also discuss the *Joule-Kelvin* throttling process and how real gas can be *liquefied*

The Joule expansion (again)

Irreversible process

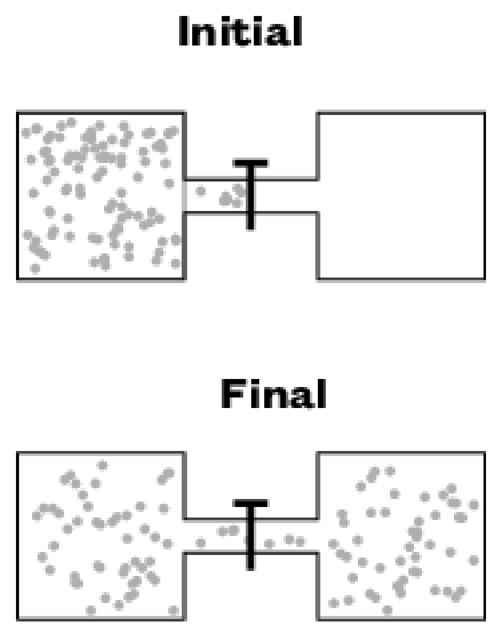
Reminder:

(1) We have an isolated system (no heat in or out)

(2) No work done either

Effect of intermolecular interactions ?

Does the gas warm, cool, or remain at constant T?



$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

Joule Coefficient

$$\mu_J = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T$$

$$= -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

$$dU = TdS - pdV \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Maxwell relation (*)

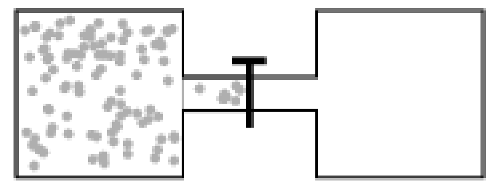
$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\mu_J = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$$

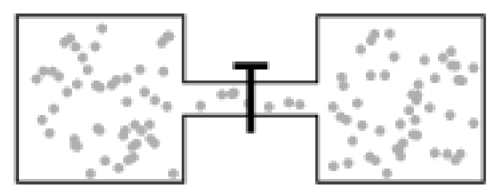
$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

Joule Coefficient

Initial



Final



$$\mu_J = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$$

Ideal gas: $p = RT/V$

$(\partial p/\partial T)_V = R/V$

$$\mu_J = 0$$

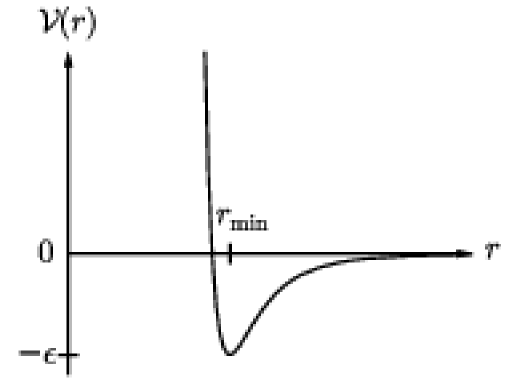
Physical Interpretation of cooling

When a gas freely expands into a vacuum, the time-averaged distance between neighboring molecules increases

Thus, the magnitude of the potential energy resulting from the attractive intermolecular interactions is reduced.

This leads to an increase in total energy

Since U is constant in a Joule expansion, the kinetic energy must be reduced and hence the temperature falls.



van der Waals gas

$$\mu_J = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$$

$$p = RT/(V-b) - a/V^2$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\mu_J = -\frac{1}{C_V}\left[\frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2}\right] = -\frac{a}{C_V V^2}$$

Temperature change:

$$\Delta T = -\frac{a}{C_V}\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V^2} = -\frac{a}{C_V}\left(\frac{1}{V_1} - \frac{1}{V_2}\right) < 0$$

Isothermal expansion

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \longrightarrow \Delta U = \int_{V_1}^{V_2}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V$$

Ideal gas: no change!

vdW gas: $\Delta U = \int_{V_1}^{V_2} \frac{a}{V^2}\,\mathrm{d}V = a(1/V_1 - 1/V_2)$ (no b dependence!)

Entropy of vdW gas

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

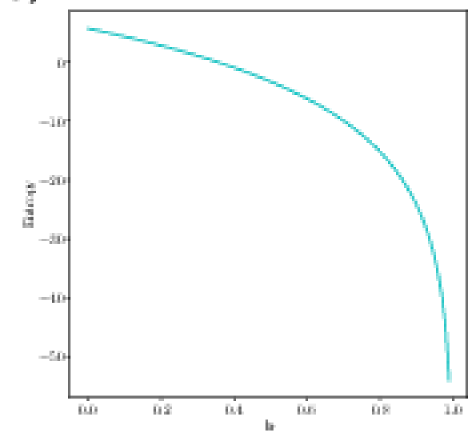
$$= \frac{C_V}{T}\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V.$$

(See chapter 16)

$(\partial p/\partial T)_V = R/(V-b)$

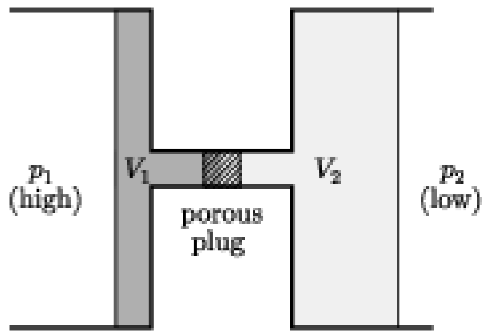
$$S = C_V \ln T + R\ln(V-b) + \text{constant}$$

$V = 1,\ T = 100,\ C_V = 1$



Only depends on *b*, not *a*, as *b* governs the number of microstates available.

Joule-Kelvin Expansion



Change in internal energy of gas moving from left to right?

(1) work done to move V_1 at p_1: p_1V_1

(2) Work to move V_2 at p_2: p_2V_2

(3) Change in internal energy is the difference between the work done on the left and on the right

$$U_1 + p_1V_1 = U_2 + p_2V_2$$

$$\longrightarrow H_1 = H_2$$ (enthalpy is conserved)

Temperature change? $\mu_{\mathrm{JK}} = \left(\frac{\partial T}{\partial p}\right)_H$

$$\mu_{\mathrm{JK}} = \left(\frac{\partial T}{\partial p}\right)_H$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \longrightarrow \mu_{\mathrm{JK}} = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T .$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \longrightarrow \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$$

$$\longrightarrow \left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

Maxwell relation (*)

$$\longrightarrow \mu_{\mathrm{JK}} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

Temperature change: $\Delta T = \int_{p_1}^{p_2} \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]\mathrm{d}p$

$$\mu_{\mathrm{J}} = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$$

Entropy Change

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p = 0 \longrightarrow \Delta S = -\int_{p_1}^{p_2} \frac{V}{T}\mathrm{d}p$$

Ideal gas: $R\ln(p_1/p_2) > 0$ (irreversible process)

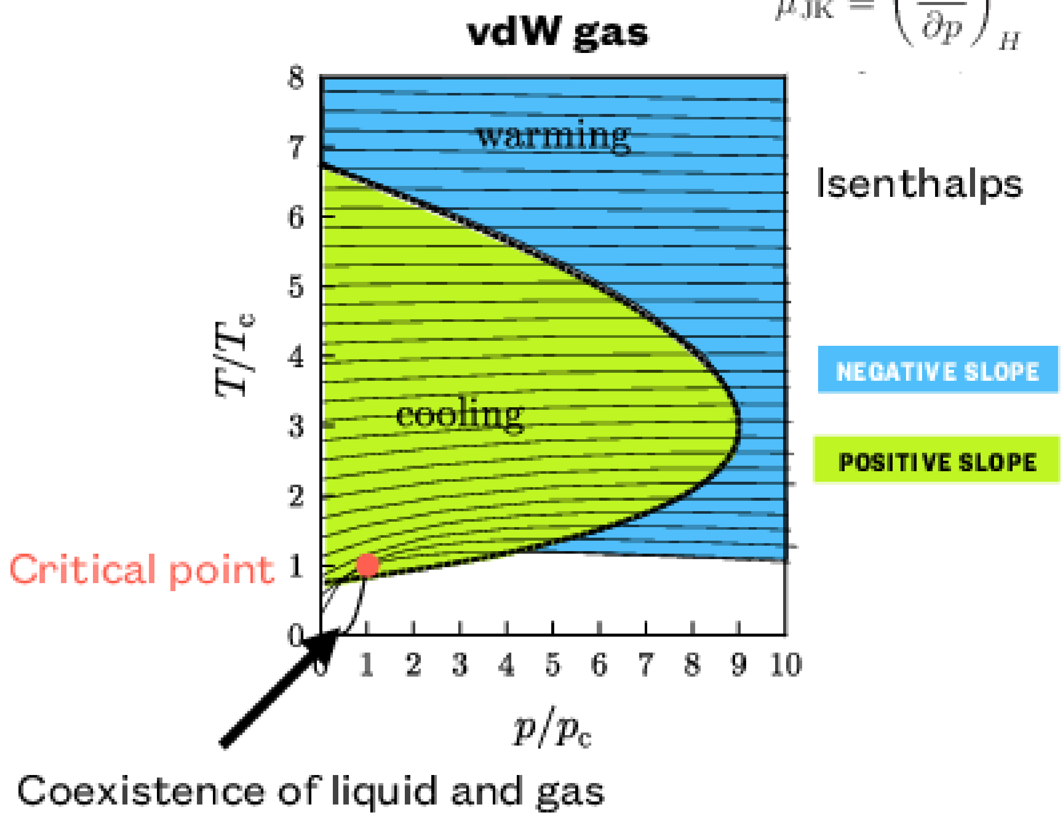
Heating or cooling?

$$\mu_{\rm JK} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

$$\mu_{\rm JK} = \left(\frac{\partial T}{\partial p}\right)_H$$

- Changes in sign when $\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}$

"Inversion curve" in the T-p plane

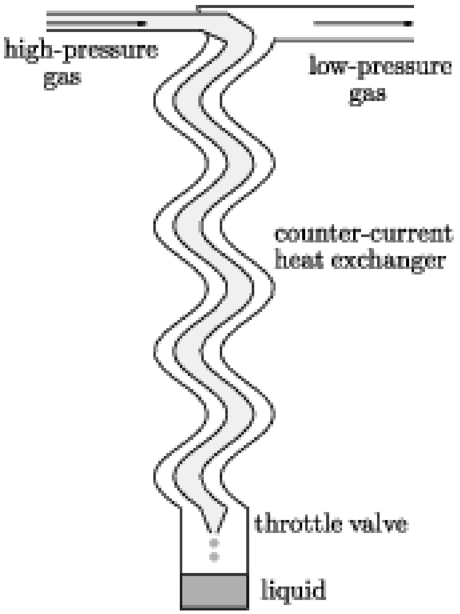


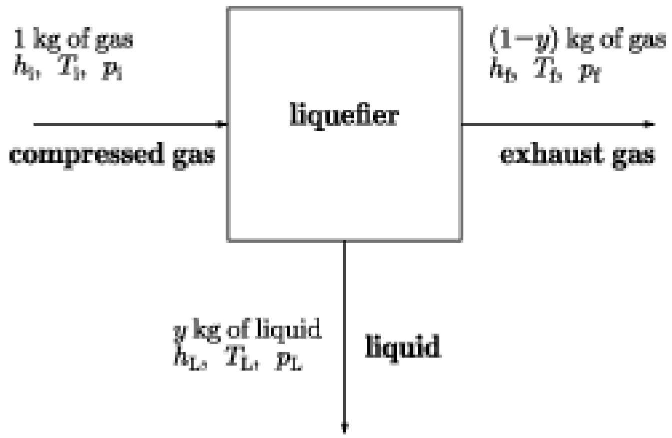
Maximum inversion temperature: under that T, JK can result in cooling

^4He	H_2	N_2	Ar	CO_2
43	204	607	794	1275

Liquefaction of gases

- Can use the JK process, but must start below the maximum inversion temperature of that gas
- High-p gas is forced through a throttle valve, and results in cooling by the JK process
- This results in low-p gas plus liquid
- Counter current heat exchanger where the outing cold low-pressure gas is used to precool the incoming warm high-pressure gas (and stay under the maximum inversion temperature)





Enthalpy is conserved, thus:

$$h_\mathrm{i} = yh_\mathrm{L} + (1-y)h_\mathrm{f}.$$

Efficiency:

$$y = \frac{h_\mathrm{f} - h_\mathrm{i}}{h_\mathrm{f} - h_\mathrm{L}}$$

For an efficient heat exchanger, T_i (compressed gas) and T_f (exhaust gas) will be the same

p_f=1 atm, TL is fixed (because it is in equilibrium with its vapor)

Thus h_f and h_L are fixed, we can only vary h_i and maximum y is found for:

$$\left(\frac{\partial h_\mathrm{i}}{\partial p_\mathrm{i}}\right)_{T_\mathrm{i}} = 0$$

$$(\partial h/\partial p)_T = -C_p\mu_\mathrm{JK} \longrightarrow \mu_\mathrm{JK} = 0.$$

We get highest efficiency on the inversion curve!

Summary

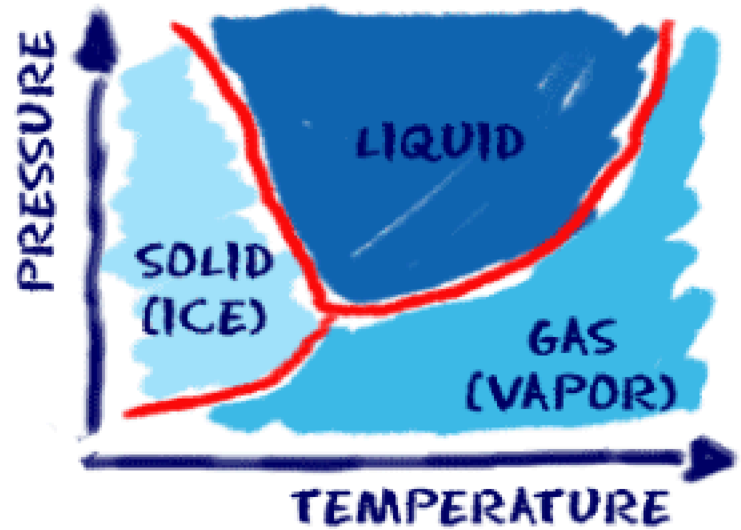
Joule expansion results in cooling for non-ideal gases because of the attractive interactions between molecules.

The entropy of a gas depends on the non-zero size of molecules.

The Joule-Kelvin expansion is a steady flow process in which enthalpy is conserved. It can result in either warming or cooling of a gas. It forms the basis of many gas liquefaction techniques.

Lecture 28. *Phase transitions*

- In this lecture, we will dig deeper into phase transitions and will study how the thermodynamics of a phase transition can be characterized using various criteria
- Exceptionally, this lecture will be provided in two parts with the second part of the screencast devoted to the so-called *Ising model*, an example of a simple system to study phase transition.



http://www.chem4kids.com/files/matter_changes.html