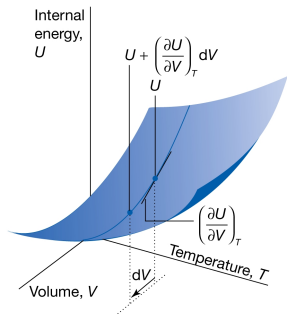


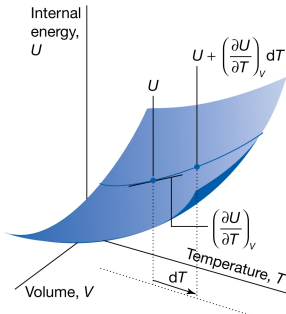
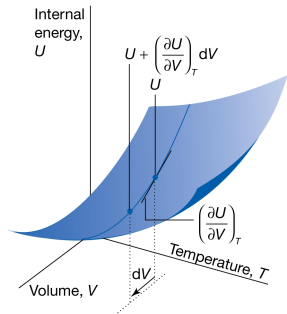
for $f \equiv f(x, y)$

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$



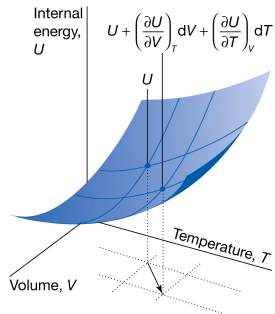
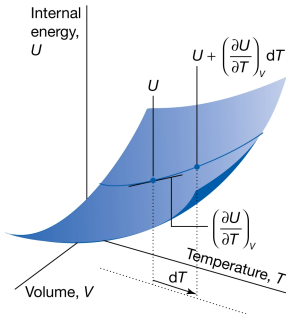
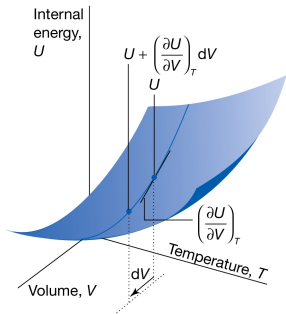
for $f \equiv f(x, y)$

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$



for $f \equiv f(x, y)$

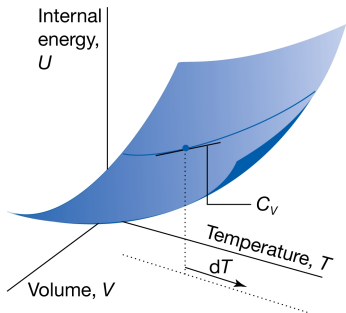
$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$



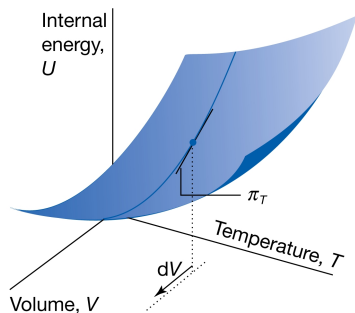
Real systems :

heat capacity at constant volume

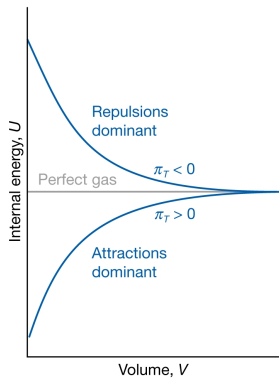
$$: C_V = \left(\frac{\partial U}{\partial T} \right)_V$$



internal pressure : $\Pi_T = \left(\frac{\partial U}{\partial V} \right)_T$



If $\Delta U > 0$ as $\Delta V > 0$ isothermally when there are attractive forces between the particles then a plot of U against V slopes upwards and $\pi_T > 0$



Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other evacuated

Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other evacuated

measured ΔT of water when a stopcock was opened and air expanded into a vacuum. He observed $\Delta T = 0$

Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other evacuated

measured ΔT of water when a stopcock was opened and air expanded into a vacuum. He observed $\Delta T = 0$

experimental limitations

Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other evacuated

measured ΔT of water when a stopcock was opened and air expanded into a vacuum. He observed $\Delta T = 0$

experimental limitations

No work done $w = 0$

No energy entered or left the system as heat because the temperature of the bath did not change, so $q = 0$

Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other evacuated

measured ΔT of water when a stopcock was opened and air expanded into a vacuum. He observed $\Delta T = 0$

experimental limitations

No work done $w = 0$

No energy entered or left the system as heat because the temperature of the bath did not change, so $q = 0$

within experimental accuracy, $\Delta U = 0$ and

$\therefore \pi_T = 0$

Joule-experiment

Joule : could we measure π_T by observing the ΔT for a gas when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other evacuated

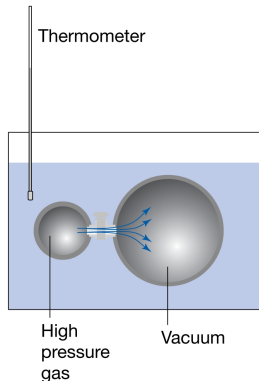
measured ΔT of water when a stopcock was opened and air expanded into a vacuum. He observed $\Delta T = 0$

experimental limitations

No work done $w = 0$

No energy entered or left the system as heat because the temperature of the bath did not change, so $q = 0$

within experimental accuracy, $\Delta U = 0$ and $\therefore \pi_T = 0$ (incorrect result)



some important relations :

some important relations :

$$U \equiv U(V, T)$$

some important relations :

$$U \equiv U(V, T)$$

$$\therefore dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$

some important relations :

$$U \equiv U(V, T)$$
$$\therefore dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$
$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

some important relations :

$$U \equiv U(V, T)$$
$$\therefore dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

def. : expansion coefficient, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$,

some important relations :

$$U \equiv U(V, T)$$

$$\therefore dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

def. : expansion coefficient, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$, then, $\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$

some important relations :

$$U \equiv U(V, T)$$

$$\therefore dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

def. : expansion coefficient, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$, then, $\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$

show : $\alpha = \frac{1}{T}$ for perfect gas

some important relations :

$$U \equiv U(V, T)$$

$$\therefore dU = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

def. : expansion coefficient, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$, then, $\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$

show : $\alpha = \frac{1}{T}$ for perfect gas

Also, for a perfect gas, $\pi_T = 0$, $\therefore \left(\frac{\partial U}{\partial T}\right)_p = C_V$

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial [U + pV]}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

$$\begin{aligned}
 C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial[U+pV]}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\
 &= (\alpha\pi_T V + C_V) + p\left(\frac{\partial V}{\partial T}\right)_p - C_V = \alpha\pi_T V + p\left(\frac{\partial V}{\partial T}\right)_p
 \end{aligned}$$

$$\begin{aligned}
 C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial[U+pV]}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\
 &= (\alpha\pi_T V + C_V) + p\left(\frac{\partial V}{\partial T}\right)_p - C_V = \alpha\pi_T V + p\left(\frac{\partial V}{\partial T}\right)_p
 \end{aligned}$$

For perfect gas, $C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p = nR$

$$\begin{aligned}
 C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial[U+pV]}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\
 &= (\alpha \pi_T V + C_V) + p \left(\frac{\partial V}{\partial T}\right)_p - C_V = \alpha \pi_T V + p \left(\frac{\partial V}{\partial T}\right)_p
 \end{aligned}$$

For perfect gas, $C_p - C_V = p \left(\frac{\partial V}{\partial T}\right)_p = nR$

Generally, $p \left(\frac{\partial V}{\partial T}\right)_p = \alpha pV$ and $C_p - C_V = \alpha(p + \pi_T) V$

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = -\left(\frac{\partial z}{\partial y}\right)_x dy_z$$

$$\text{or, } \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x, \implies \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$H \equiv H(p, T) \implies$$

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

$$\text{or, } \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x, \implies \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$H \equiv H(p, T) \implies dH = \underbrace{\left(\frac{\partial H}{\partial p}\right)_T}_{\downarrow} dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

$$\text{or, } \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x, \implies \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$H \equiv H(p, T) \implies dH = \underbrace{\left(\frac{\partial H}{\partial p}\right)_T}_{\downarrow} dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$-\frac{1}{\underbrace{\left(\frac{\partial p}{\partial T}\right)_H}_{\mu} \underbrace{\left(\frac{\partial T}{\partial H}\right)_p}} = - \underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\mu} \left(\frac{\partial H}{\partial T}\right)_p$$

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

$$\text{or, } \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x, \implies \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$H \equiv H(p, T) \implies dH = \underbrace{\left(\frac{\partial H}{\partial p}\right)_T}_{\downarrow} dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$-\frac{1}{\underbrace{\left(\frac{\partial p}{\partial T}\right)_H}_{\underbrace{\hspace{1cm}}_p} \underbrace{\left(\frac{\partial T}{\partial H}\right)_p}_p} = - \underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\substack{\uparrow \\ \mu}} \left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p$$

J T coefficient

$$z = f(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

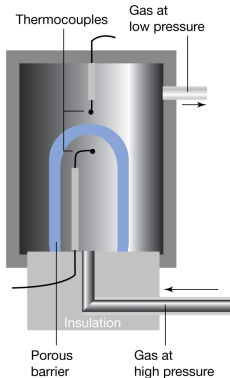
$$\text{or, } \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x, \implies \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$H \equiv H(p, T) \implies dH = \underbrace{\left(\frac{\partial H}{\partial p}\right)_T}_{\downarrow} dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$-\frac{1}{\underbrace{\left(\frac{\partial p}{\partial T}\right)_H}_{\mu} \underbrace{\left(\frac{\partial T}{\partial H}\right)_p}_p} = - \underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\substack{\mu \\ \uparrow \\ \text{J T coefficient}}} \left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p$$

$$\therefore dH = -\mu C_p dp + C_p dT$$

Joule-Thomson coefficient - apparatus



let a gas expand through a porous barrier from one constant pressure to another

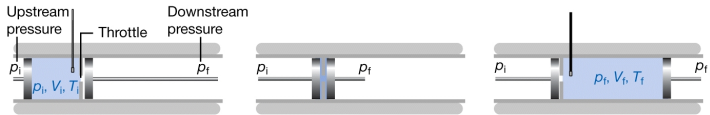
monitor the difference of temperature that arises from expansion

whole apparatus is insulated : adiabatic
 $q = 0 \implies \Delta U = w$

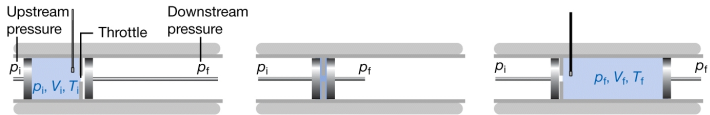
observed lower temperature on low pressure side, $\Delta T \propto$ pressure difference

Joule-Thomson effect : cooling by isenthalpic expansion

Joule-Thomson coefficient - thermodynamic basis



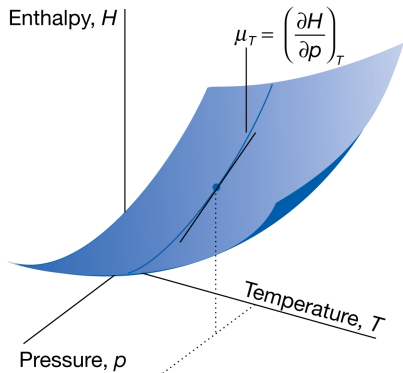
Joule-Thomson coefficient - thermodynamic basis



$$\Delta U = U_f - U_i = w = w_1 + w_2 = -p_i (0 - V_i) - p_f (V_f - 0) = p_i V_i - p_f V_f$$

$$\therefore U_f + p_f V_f = U_i + p_i V_i = \text{const } H$$

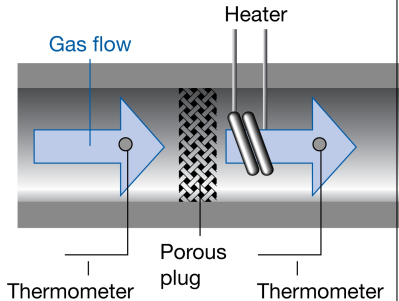
isothermal Joule-Thomson coefficient, $\mu_T = \left(\frac{\partial H}{\partial p} \right)_T = -C_p \mu$



isothermal Joule-Thomson coefficient, $\mu_T = \left(\frac{\partial H}{\partial p} \right)_T = -C_p \mu$

Isothermal Joule-Thomson coefficient - measurement

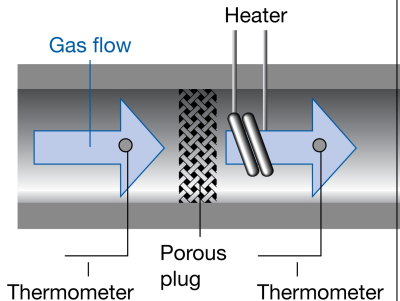
gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)



Isothermal Joule-Thomson coefficient - measurement

gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)

then through a porous plug inside a thermally insulated container

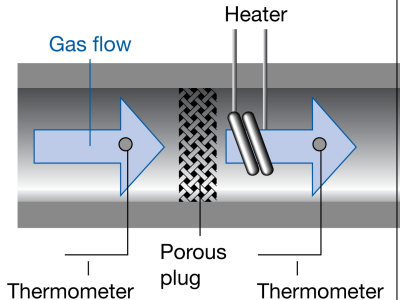


Isothermal Joule-Thomson coefficient - measurement

gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)

then through a porous plug inside a thermally insulated container

steep pressure drop is measured, and cooling effect is exactly offset by an electric heater placed immediately after the plug

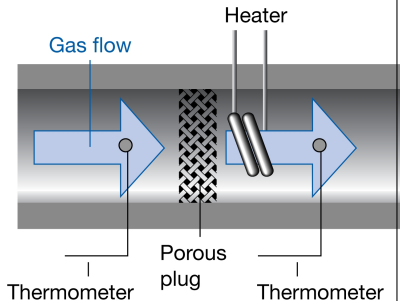


Isothermal Joule-Thomson coefficient - measurement

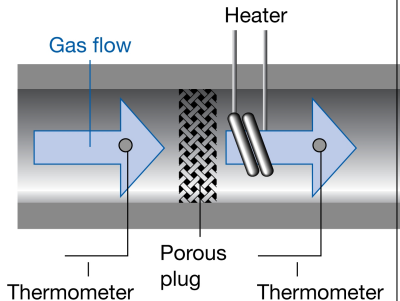
gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)

then through a porous plug inside a thermally insulated container

steep pressure drop is measured, and cooling effect is exactly offset by an electric heater placed immediately after the plug
energy provided by the heater is monitored



Isothermal Joule-Thomson coefficient - measurement



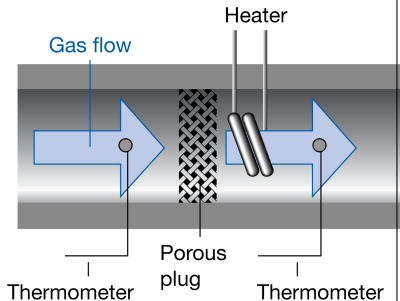
gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)

then through a porous plug inside a thermally insulated container

steep pressure drop is measured, and cooling effect is exactly offset by an electric heater placed immediately after the plug

energy provided by the heater is monitored
energy transferred as heat = ΔH_p

Isothermal Joule-Thomson coefficient - measurement



gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)

then through a porous plug inside a thermally insulated container

steep pressure drop is measured, and cooling effect is exactly offset by an electric heater placed immediately after the plug

energy provided by the heater is monitored
energy transferred as heat = ΔH_p

find $\mu_T = \lim_{p \rightarrow 0} \mathcal{L} t \frac{\Delta H}{\Delta p}$ and convert to μ

- ▶ Real gases have nonzero J T coefficients

- ▶ Real gases have nonzero J T coefficients
- ▶ speed of molecules $\propto T$
- ▶ reducing average speed is equivalent to cooling

- ▶ Real gases have nonzero J/T coefficients
- ▶ speed of molecules $\propto T$
- ▶ reducing average speed is equivalent to cooling
- ▶ If speed is reduced to the point that neighbours can capture each other by intermolecular attractions, then it condenses to a liquid
- ▶ Sign of μ depends on the gas, p , relative magnitudes of attractive and repulsive forces and T

- ▶ Real gases have nonzero J/T coefficients
- ▶ speed of molecules $\propto T$
- ▶ reducing average speed is equivalent to cooling
- ▶ If speed is reduced to the point that neighbours can capture each other by intermolecular attractions, then it condenses to a liquid
- ▶ Sign of μ depends on the gas, p , relative magnitudes of attractive and repulsive forces and T
- ▶ if molecules are moved away from each other, then they should slow
 - ▶ Allow the gas to expand, which increases average separation

- ▶ Real gases have nonzero J/T coefficients
- ▶ speed of molecules $\propto T$
- ▶ reducing average speed is equivalent to cooling
- ▶ If speed is reduced to the point that neighbours can capture each other by intermolecular attractions, then it condenses to a liquid
- ▶ Sign of μ depends on the gas, p , relative magnitudes of attractive and repulsive forces and T
- ▶ if molecules are moved away from each other, then they should slow
 - ▶ Allow the gas to expand, which increases average separation
- ▶ To cool a gas, allow it to expand without allowing any energy to enter from outside as heat

molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours

molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours
- ▶ some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: the cooling of a real gas by adiabatic expansion.

molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours
- ▶ some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: the cooling of a real gas by adiabatic expansion.
- ▶ $\mu > 0 \implies dT < 0$ when $dp < 0 \implies$

molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours
- ▶ some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: the cooling of a real gas by adiabatic expansion.
- ▶ $\mu > 0 \implies dT < 0$ when $dp < 0 \implies$ gas cools on expansion, attractive interactions dominant - molecules have to climb apart against attractive force in order to travel more slowly

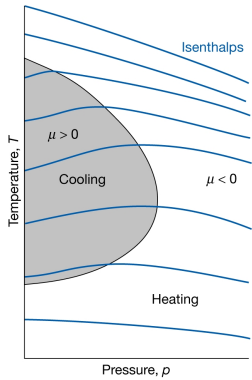
molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours
- ▶ some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: the cooling of a real gas by adiabatic expansion.
- ▶ $\mu > 0 \implies dT < 0$ when $dp < 0 \implies$ gas cools on expansion, attractive interactions dominant - molecules have to climb apart against attractive force in order to travel more slowly
- ▶ when repulsions are dominant, $Z > 1$: heating effect

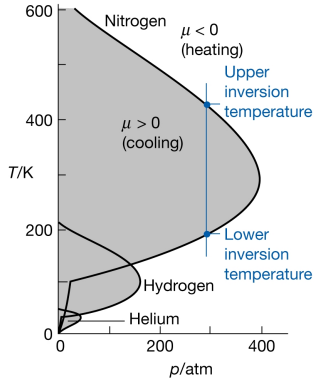
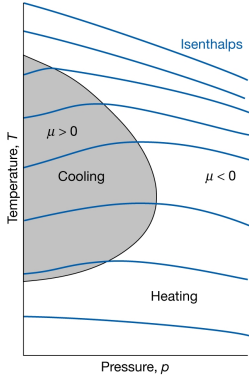
molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours
- ▶ some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: the cooling of a real gas by adiabatic expansion.
- ▶ $\mu > 0 \implies dT < 0$ when $dp < 0 \implies$ gas cools on expansion, attractive interactions dominant - molecules have to climb apart against attractive force in order to travel more slowly
- ▶ when repulsions are dominant, $Z > 1$: heating effect
- ▶ typically there are two inversion temperatures, one at high temperature and other at low : $\mu < 0$ at one temperature
 - ▶ and cooling effect $\mu > 0$ when $T < \text{upper inversion temperature}$

Inversion temperature :

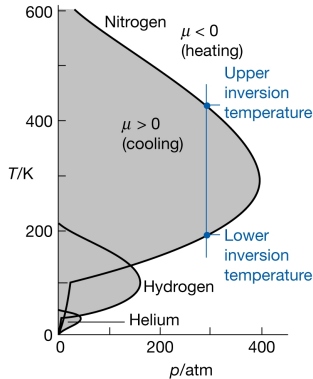
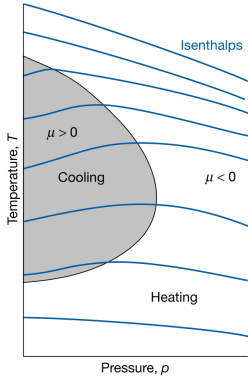


Inversion temperature :



Inversion temperature corresponds to the boundary at a given pressure

Inversion temperature :

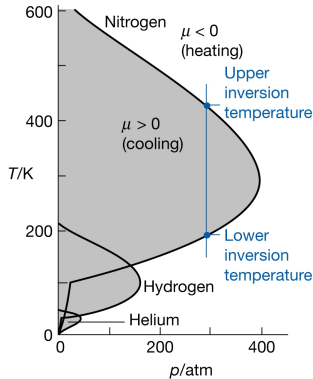
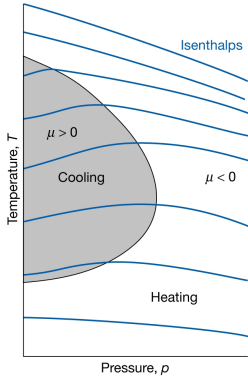


Inversion temperature corresponds to the boundary at a given pressure

For a given pressure, temperature must be below a certain value if cooling is required

but, if it becomes too low, the boundary is crossed again and heating occurs

Inversion temperature :

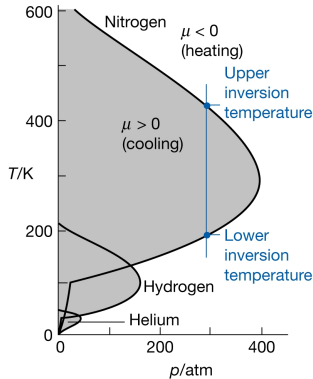
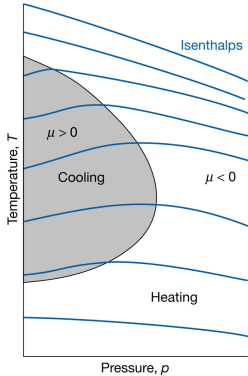


Inversion temperature corresponds to the boundary at a given pressure

For a given pressure, temperature must be below a certain value if cooling is required

but, if it becomes too low, the boundary is crossed again and heating occurs
Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy

Inversion temperature :



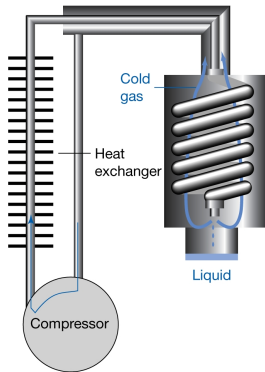
Inversion temperature corresponds to the boundary at a given pressure

For a given pressure, temperature must be below a certain value if cooling is required

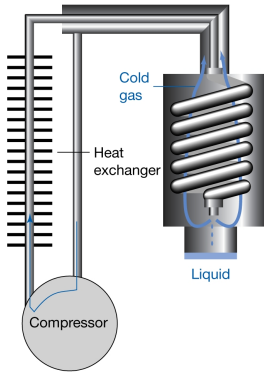
but, if it becomes too low, the boundary is crossed again and heating occurs
Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy

inversion temperature curve runs through points of isenthalps where their slope changes from negative to positive

Linde Refrigerator for liquefying gases

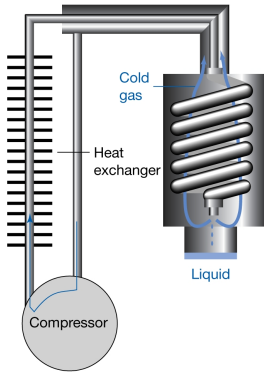


Linde Refrigerator for liquefying gases



gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas

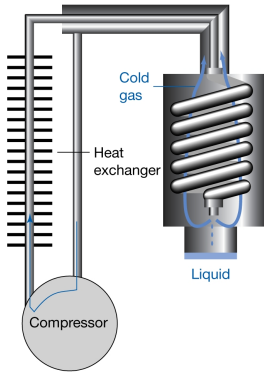
Linde Refrigerator for liquefying gases



gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas

That gas is cooled, and its subsequent expansion cools it still further

Linde Refrigerator for liquefying gases



gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas

That gas is cooled, and its subsequent expansion cools it still further

There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

- ▶ For a perfect gas, $\mu = 0$

- ▶ For a perfect gas, $\mu = 0$
- ▶ \therefore temperature of perfect gas is unchanged by J T expansion

- ▶ For a perfect gas, $\mu = 0$
- ▶ \therefore temperature of perfect gas is unchanged by J T expansion
- ▶ However, μ for a real gas does not necessarily approach zero as p is reduced even though equation of state approaches that of a perfect gas

- ▶ For a perfect gas, $\mu = 0$
- ▶ \therefore temperature of perfect gas is unchanged by J T expansion
- ▶ However, μ for a real gas does not necessarily approach zero as p is reduced even though equation of state approaches that of a perfect gas
- ▶ The coefficient depends on derivatives and not on p , V and T themselves

Second law :

Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work

Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work

Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work
- ▶ Clausius : It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher temperature sink

Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work
- ▶ Clausius : It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher temperature sink
- ▶ Carnot : No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. The efficiency of an engine can never be 100%

Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work
- ▶ Clausius : It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher temperature sink
- ▶ Carnot : No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. The efficiency of an engine can never be 100%
- ▶ Entropy principle : Entropy of universe (System+surroundings) always increases in a natural (spontaneous) process

Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work
- ▶ Clausius : It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher temperature sink
- ▶ Carnot : No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. The efficiency of an engine can never be 100%
- ▶ Entropy principle : Entropy of universe (System+surroundings) always increases in a natural (spontaneous) process
- ▶ Clausius inequality : $\Delta S \geq \int \frac{dq}{T}$ neighbourhood

Second law :

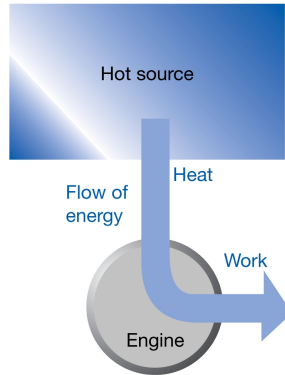
- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work
- ▶ Clausius : It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher temperature sink
- ▶ Carnot : No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. The efficiency of an engine can never be 100%
- ▶ Entropy principle : Entropy of universe (System+surroundings) always increases in a natural (spontaneous) process
- ▶ Clausius inequality : $\Delta S \geq \int \frac{dq}{T}$ neighbourhood
- ▶ Caratheodory axiom : In the neighbourhood of any arbitrary initial state of a physical system, P_0 , there exist neighbouring states that are not accessible from P_0 along reversible adiabatic paths

Thermodynamic engine : device that allows a system to draw heat from a source, convert part of it into work and dump unused heat to a sink

Thermodynamic engine : device that allows a system to draw heat from a source, convert part of it into work and dump unused heat to a sink

Second law : complete conversion
of heat into work impossible

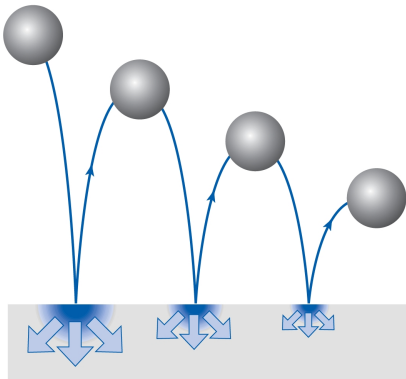
Thermodynamic engine : device that allows a system to draw heat from a source, convert part of it into work and dump unused heat to a sink



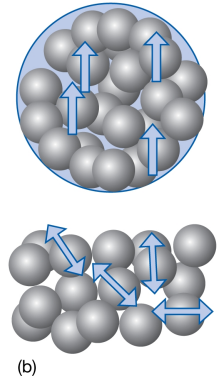
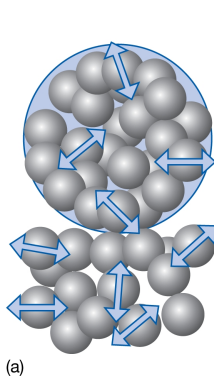
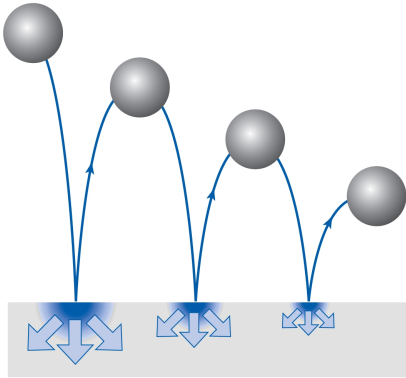
Second law : complete conversion
of heat into work impossible

NOT POSSIBLE

Heat and work : molecular understanding



Heat and work : molecular understanding



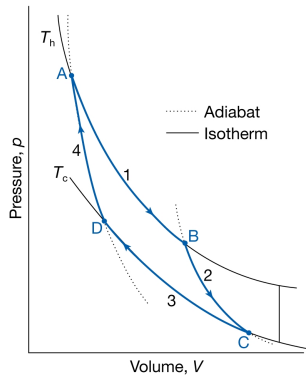
spontaneous change: direction of change leading to dispersal of total energy of isolated systems

Entropy : $dS = \int \frac{dq_{\text{rev}}}{T}$ and $\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$

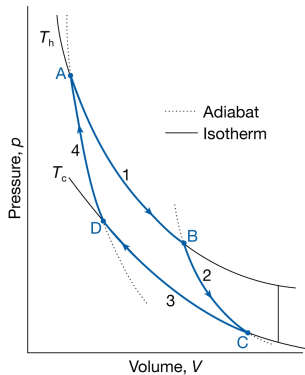
isothermal expansion : $\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{-w_{\text{rev}}}{T} = nR \ln \frac{V_f}{V_i}$

adiabatic process : $\Delta S = 0$

Carnot cycle : a model - perfect gas as fuel for an engine



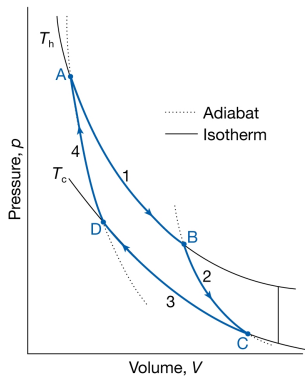
Carnot cycle : a model - perfect gas as fuel for an engine



1. Reversible isothermal expansion from A to B
at T_h ; $\Delta S = \frac{q_h}{T_h}$;

where q_h = energy supplied from hot source > 0

Carnot cycle : a model - perfect gas as fuel for an engine



1. Reversible isothermal expansion from A to B
at T_h ; $\Delta S = \frac{q_h}{T_h}$;

where q_h = energy supplied from hot source > 0

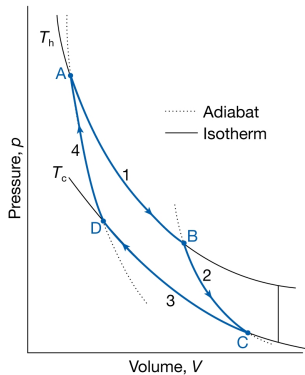
2. Reversible adiabatic expansion from B to C
 $\Delta S = 0$; $\Delta T = -(T_h - T_c)$

3. Reversible isothermal compression from C to
D at T_c ; $\Delta S = \frac{q_c}{T_c}$

Energy released as heat to the cold sink < 0

4. Reversible adiabatic compression from D to A
 $\Delta S = 0$; $\Delta T = T_h - T_c$

Carnot cycle : a model - perfect gas as fuel for an engine



1. Reversible isothermal expansion from A to B
at T_h ; $\Delta S = \frac{q_h}{T_h}$;

where q_h = energy supplied from hot source > 0

2. Reversible adiabatic expansion from B to C
 $\Delta S = 0$; $\Delta T = -(T_h - T_c)$

3. Reversible isothermal compression from C to
D at T_c ; $\Delta S = \frac{q_c}{T_c}$

Energy released as heat to the cold sink < 0

4. Reversible adiabatic compression from D to A
 $\Delta S = 0$; $\Delta T = T_h - T_c$

Total $\Delta S = \oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$