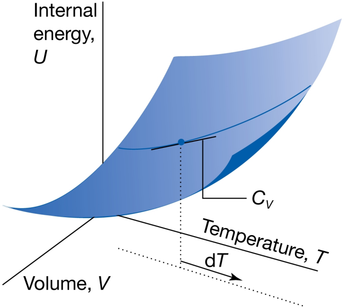
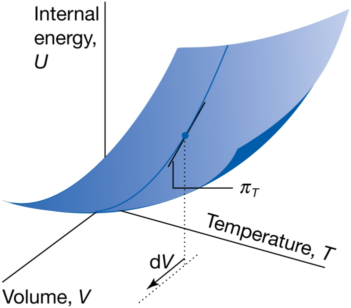
Real systems :

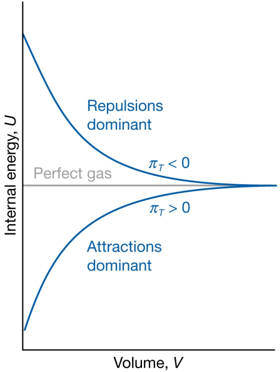
heat capacity at constant volume : $C_V = \left(\frac{\partial U}{\partial T}\right)_V$



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 $\pi_T > 0$



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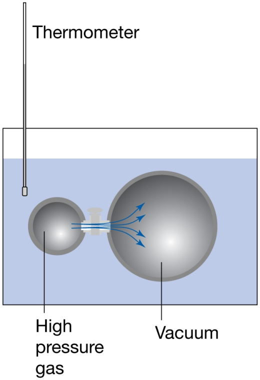

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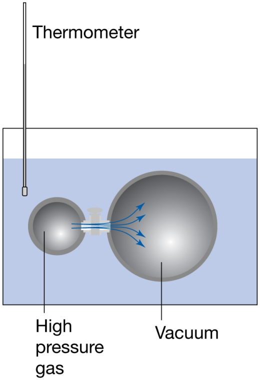

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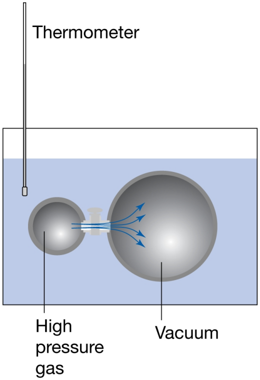

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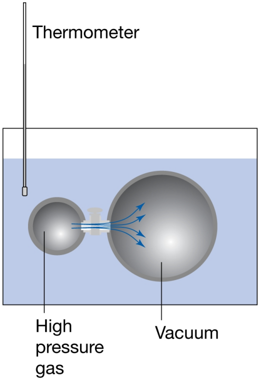

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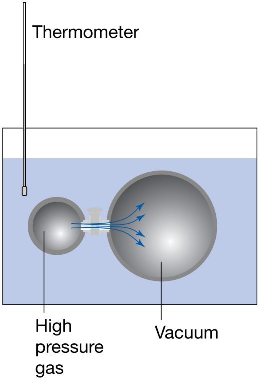

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Also, for a perfect gas, $\pi_T = 0$, $\quad \therefore \left(\frac{\partial U}{\partial T}\right)_p = C_V$

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

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J T coefficient

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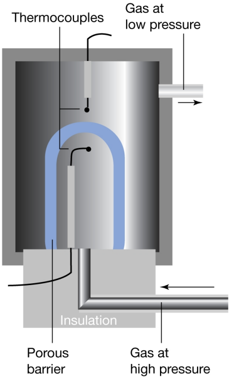
J T coefficient

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

Joule-Thomson coefficient - apparatus



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

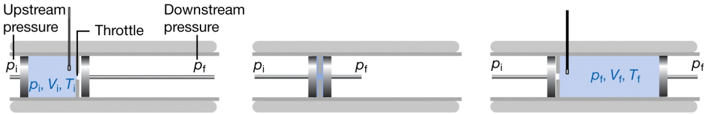
monitor the difference of temperature that arises from expansion

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



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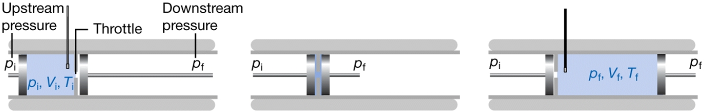

$$\Delta U = U_f - U_i = w = w_1 + w_2$$

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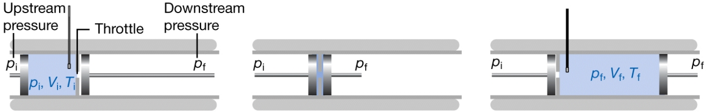

$$\Delta U = U_f - U_i = w = w_1 + w_2 = -p_i\,(0 - V_i) - p_f\,(V_f - 0)$$

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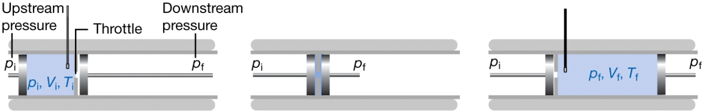

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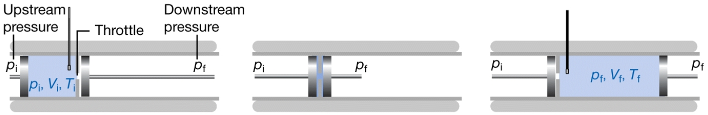

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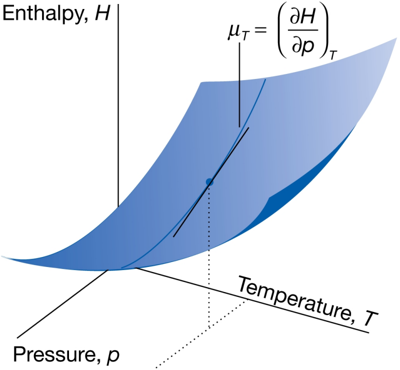
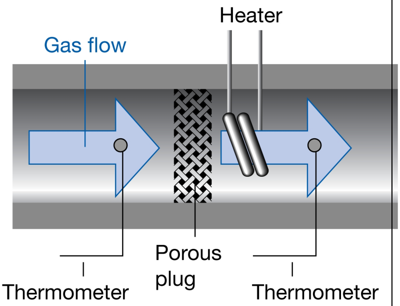
$$\therefore\ U_f + p_f V_f = U_i + p_i V_i = \text{const } H$$

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



Isothermal Joule-Thomson coefficient - measurement



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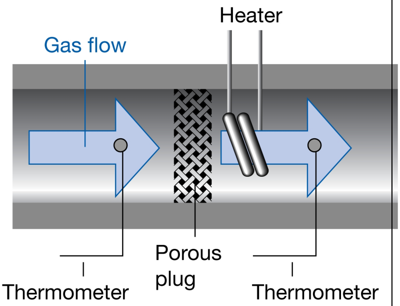

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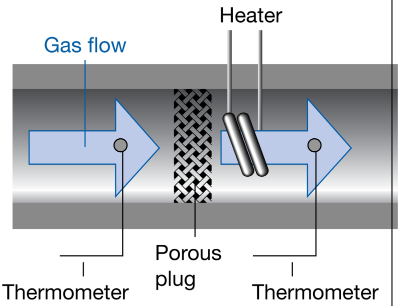

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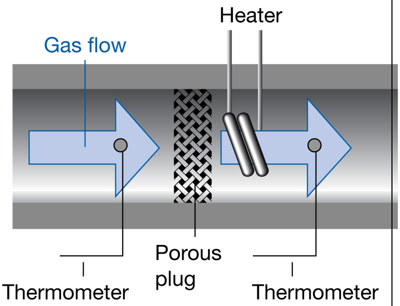

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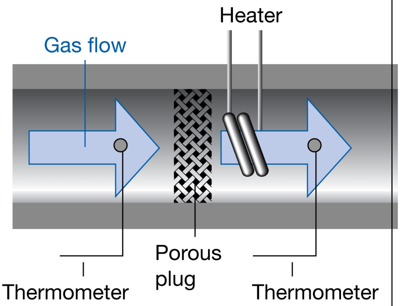

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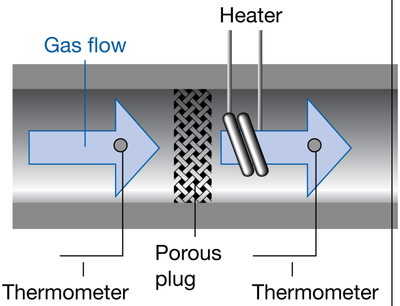

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find $\mu_T = \underset{p \to 0}{\mathcal{L}t} \frac{\Delta H}{\Delta p}$ and convert to μ

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- if molecules are moved away from each other, then they should slow
  - Allow the gas to expand, which increases average separation

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- 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

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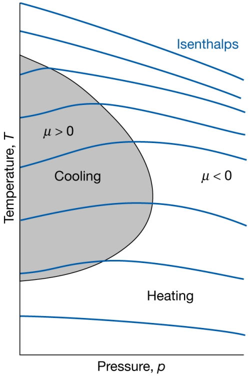
- inversion temperature : Where the shift in behaviour occurs (cooling to heating with lowering pressure).
- typically there are two inversion temperatures, one at high temperature and other at low : $\mu < 0$ at some temperatures
  - and cooling effect $\mu > 0$ when $T <$ upper inversion temperature

Inversion temperature :



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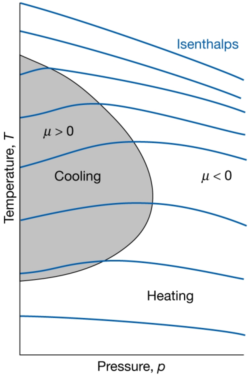

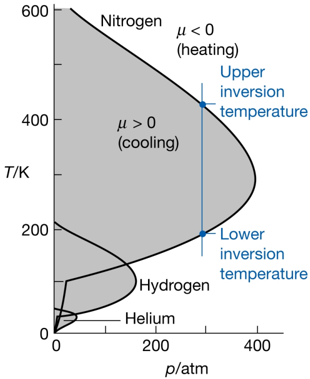

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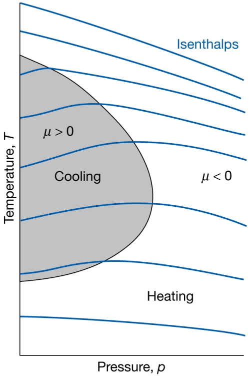

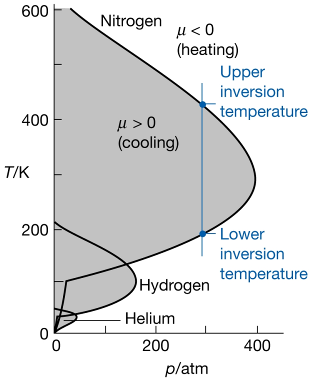

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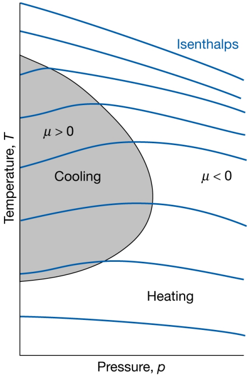

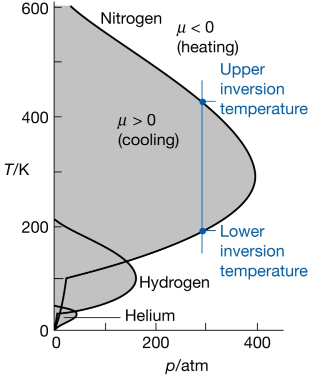

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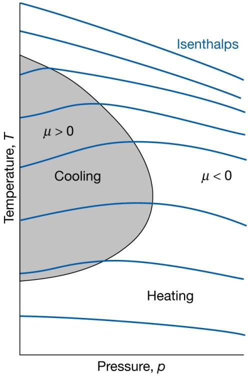

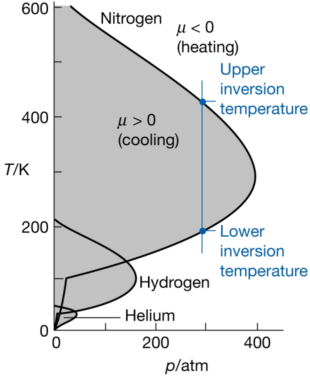

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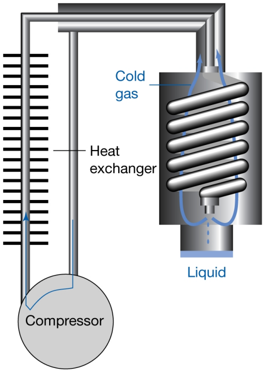
inversion temperature curve runs through points of isenthalps where their slope changes from negative to positive

Linde Refrigerator for liquefying gases



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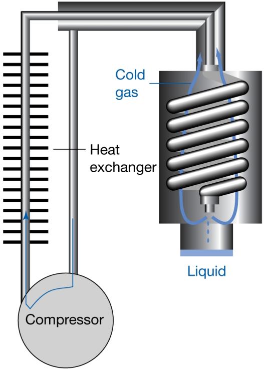

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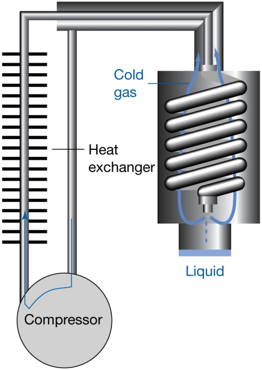

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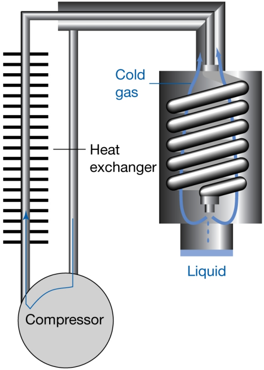

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There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

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- 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

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- 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

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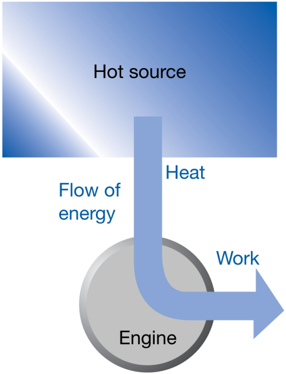

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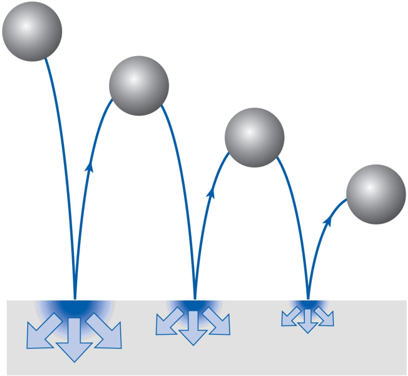
NOT POSSIBLE

Heat and work : molecular understanding



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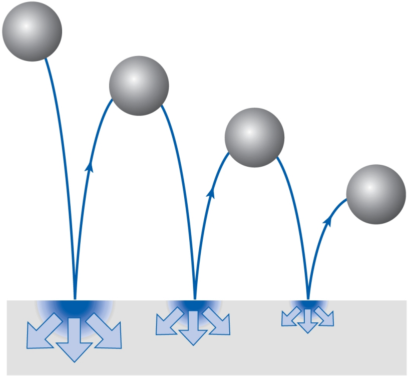
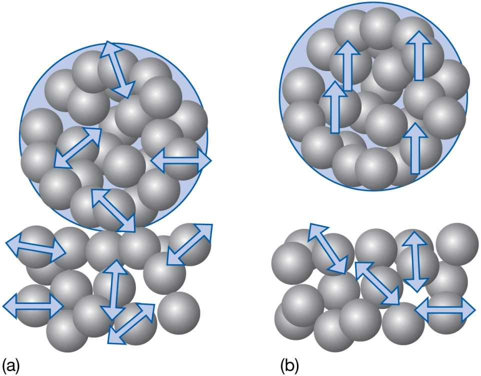




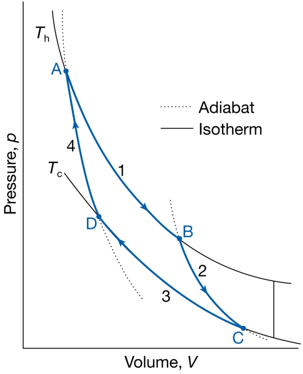
spontaneous change: direction of change leading to dispersal of total energy of isolated systems

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

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

adiabatic process : $\Delta S = 0$

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



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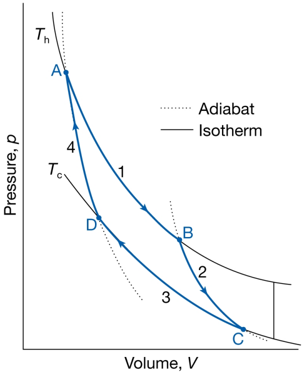

1. Reversible isothermal expansion from A to B at T_h; $\Delta S = \frac{q_h}{T_h}$;

where q_h = energy supplied from hot source > 0

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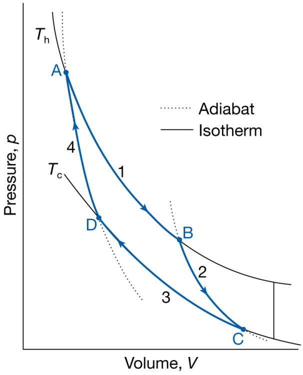

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3. Reversible isothermal compression from C to D at T_c; $\Delta S = \frac{q_c}{T_c}$

Energy released as heat to the cold sink < 0

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

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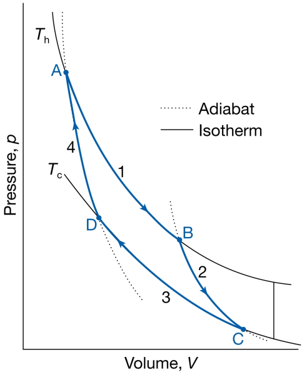

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Total $\Delta S = \oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$