TB 13.12 Joule-Kelvin 02-01-18

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Initialization: Be sure the file *NTGUtilityFunctions.m* is in the same directory as that from which this notebook was loaded. Then execute the cell immediately below by mousing left on the cell bar to the right of that cell and then typing "shift" + "enter". Respond "Yes" in response to the query to evaluate initialization cells.

```
SetDirectory[NotebookDirectory[]];
 (* set directory where source files are located *)
Get["NTGUtilityFunctions.m"]; (* Load utilities package *)
```

Purpose

This is the 7th in a series of notebooks in which I work through material and exercises in the magisterial new book *Modern Classical Physics* by Kip S. Thorne and Roger D. Blandford. If you are a physicist of any ilk, BUY THIS BOOK. You will learn from a close reading and from solving the exercises.

Exercise 13.12 *Derivation: Joule-Kelvin Coefficient*
Verify Eq. (13.60)

13.5.6 Joule-Kelvin Method of Cooling a Real Gas

Let us return to the contribution $P\mathbf{v}$ to the energy flux. A good illustration of the importance of this term is provided by the ***Joule-Kelvin method*** commonly used to cool gases (Fig. 13.7). In this method, gas is driven from a high-pressure chamber 1 through a nozzle or porous plug into a low-pressure chamber 2, where it can expand and cool. We can analyze the cooling using energy conservation, with the magnitude of the energy flux at the entrance to the nozzle written as $(\rho_1 u_1 + P_1)v_1$ (where we neglect the kinetic energy and gravitational terms as negligible). During a short time Δt, the energy that leaves the high-pressure chamber 1 is this energy flux into the nozzle times Δt times the nozzle entrance's area A_1 : $\Delta E_1 = (\rho_1 u_1 + P_1)v_1 \Delta t A_1 = H_1$; here H_1 is the enthalpy that the departing gas "sample" had when it was in chamber 1, occupying the volume $v_1 \Delta t A_1$. (Without the $P_1 v_1$ term in the flux, we would not get this result.) When this gas sample arrives in the low-pressure chamber 2, it is far from statistical (thermodynamic) equilibrium, but it soon equilibrates. After equilibration, it occupies some volume V_2, it has done work $P_2 V_2$ on the gas in chamber 2 in order to open up that volume, and it posses an internal energy $\rho_2 u_2 V_2$. Correspondingly, the total energy it has injected into chamber 2 is $\Delta E_2 = (\rho_2 u_2 + P_2)V_2 = H_2$ (its enthalpy); cf. the last part of Ex. 5.5. Energy conservation, $\Delta E_1 = \Delta E_2$, then guarantees that the enthalpy H_1 of this gas sample when it was in statistical equilibrium in chamber 1 is the same as its enthalpy H_2 when it has reached statistical equilibrium in chamber 2. Dividing by the mass of the sample, we see that *the enthalpy per unit mass, h, is the same in the two chambers:* $h_1 = h_2$.

Now, the temperature T of the gas, in statistical equilibrium, is some function of enthalpy and pressure, $T = T(h, P)$; so we can write the temperature drop between chamber 1 and chamber 2 as

$$\Delta T = \int_{P_1}^{P_2} \mu_{JK} dP, \qquad (13.59)$$

where $\mu_{JK} \equiv (\partial T/\partial P)_h$ is the so-called Joule-Kelvin coefficient. A straightforward thermodynamic calculation yields the identity

$$\mu_{JK} \equiv \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{\rho^2 c_p}\left(\frac{\partial(\rho T)}{\partial T}\right)_P. \qquad (13.60)$$

The Joule-Kelvin coefficient of an ideal gas [one with $P = n k_B T = (\rho/\mu m_p)k_B T$] obviously vanishes. Therefore, the cooling must arise because of the attractive forces (van der

Analysis and solution

Part (a)

**Fluid with mass ΔM
is adiabatically forced
through porous plug**

P
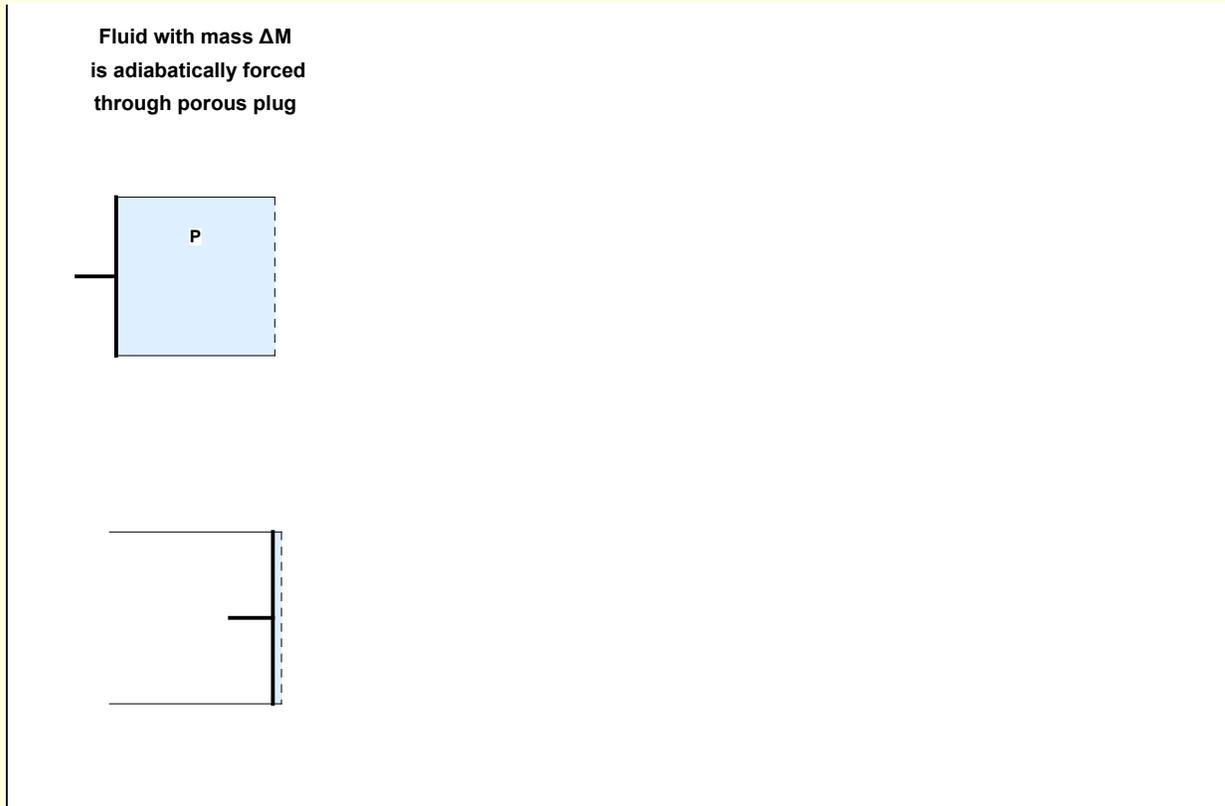
The dynamics of the energy flow are given by

$$\frac{\partial U}{\partial t} + \nabla \cdot \mathbf{F} = 0 \tag{1}$$

where is the energy density and **F** is the energy density flux**.**

$$U = \rho\left(\frac{v^2}{2} + u + \Phi\right)$$

$$\mathbf{F} = \rho\, \mathbf{v}\left(\frac{v^2}{2} + h + \Phi\right) = \rho\, \mathbf{v}\left(\frac{v^2}{2} + u + \frac{P}{\rho} + \Phi\right) \tag{2}$$

Here, h, u, etc. are "specific" quantities - the enthalpy per unit mass, the internal energy per unit mass, etc.

Imagine that a mass ΔM is forced across the porous plug in an adiabatic manner. For the situation indicated in the diagram there is no change in the level of the fluid in the gravitational field so the term Φ

is small. Also, the flow in the system is quite small compared with thermal velocities (adiabatic process) so

$$F \simeq \rho v \left(u + \frac{P}{\rho} \right) \tag{3}$$

The amount of energy associated with the outflow of ΔM is

$$\Delta E = \rho \left(u + \frac{P}{\rho} \right)(v A \, \Delta t) = \text{(energy density)} \, \text{(volume occupied by } \Delta m) \tag{4}$$
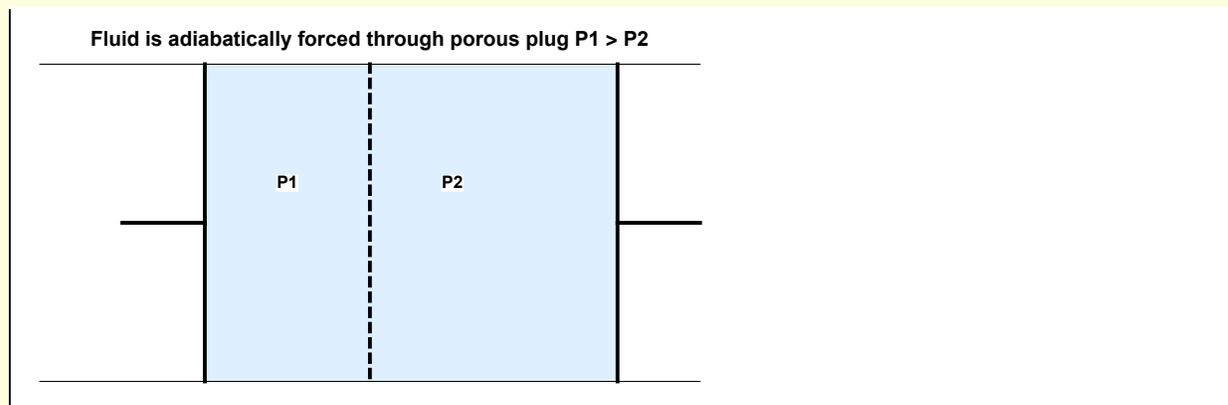
Also

$$\Delta E = \rho \left(u + \frac{P}{\rho} \right)(v A \, \Delta t) = \left(u + \frac{P}{\rho} \right)(\rho v A \, \Delta t) = h \, \Delta M \tag{5}$$

where h is the specific enthalpy. Thus

$$\Delta E = h \, \Delta M \equiv \Delta H \tag{6}$$

For this outflow, the change in energy is equal to change in enthalpy.

Part (b)

Fluid is adiabatically forced through porous plug P1 > P2

The change in the energy as a fluid element with mass M passes through the plug from region 1 to region 2 and equilibrates is

$$\Delta U = \Delta W + \Delta Q = \Delta W \tag{7}$$

because the process is adiabatic, ΔQ = 0. Then

$$\Delta U = U_2 - U_1 = \Delta W \tag{8}$$

It is important to get the sign right when calculating the work. On the left work is performed on the fluid to force it through the porous plug. The work performed on the fluid was

$$W_1 = P_1 V_1 > 0 \tag{9}$$

where V_1 is the volume of the fluid element with mass M.

In region 2, the fluid element performed work on the environment in order to make space for itself.

$$W_2 = P_2 V_2 < 0 \tag{10}$$

The net positive work that has been performed is

$$\Delta W = W_1 - W_2 = P_1 V_1 - P_2 V_2 > 0 \tag{11}$$

Thus

$$\Delta U = U_2 - U_1 = \Delta W = P_1 V_1 - P_2 V_2 \tag{12}$$

or

$$U_2 + P_2 V_2 = U_1 + P_1 V_1 \tag{13}$$

or

$$H_2 = H_1 \tag{14}$$

Enthalpy is conserved.

Part (c)

The problem calls for the derivation of an explicit form for

$$\mu_{JT} \equiv \frac{\partial T}{\partial P}\bigg|_H \tag{15}$$

Define some quantities and use the constancy of the enthalpy to obtain an expression for μ_{JT}

```
def[dH] = dH == H[P, T] - H[P0, T0];
def[dP] = dP == P - P0;
def[dT] = dT == T - T0;
def[dS] = dS == S[P, T] - S[P0, T0];
```

```
w[1] = H[P, T] == Normal@Series[H[P, T], {P, P0, 1}, {T, T0, 1}] /.
      {Sol[def[dH], H[P, T]], Sol[def[dP], P], Sol[def[dT], T]} /.
     {P0 → P, T0 → T} // Sol[#, dH] & // RE

dH == dT H^(0,1) [P, T] + dP H^(1,0) [P, T] + dP dT H^(1,1) [P, T]
```

```
w[2] = w[1] /. {dP → ε dP, dT → ε dT} /. εⁿ_/;n>1 → 0 /. ε → 1
```

$$dH == dT\ H^{(0,1)}[P,\ T] + dP\ H^{(1,0)}[P,\ T]$$

```
def[μJT] = μJT == dT / dP
```

$$\mu JT == \frac{dT}{dP}$$

```
w[3] = Sol[w[2] /. dH → 0, dT] // RE;
w[3] = MapEqn[(# / dP) &, w[3]] /. Sol[def[μJT], dP]
```

$$\mu JT == -\frac{H^{(1,0)}[P,\ T]}{H^{(0,1)}[P,\ T]}$$

The denominator is a common thermodynamic quantity, the specific heat at constant enthalpy

```
def[Cp] = Cp == H^(0,1)[P, T]
```

$$Cp == H^{(0,1)}[P,\ T]$$

```
w[4] = w[3] /. Sol[def[Cp], H^(0,1)[P, T]]
```

$$\mu JT == -\frac{H^{(1,0)}[P,\ T]}{Cp}$$

It remains to express the numerator in terms of familiar (and measurable) quantities

Proceed by making use of definition of H (differential form)

```
w[5] = dH == dU + dP V[T] + P dV
```

$$dH == dU + dV\ P + dP\ V[T]$$

and the fundamental thermodynamic relationship

```
w[6] = dU == T dS - P dV
```

$$dU == -dV\ P + dS\ T$$

Then

```
w[7] = Sol[w[6], dS] /. Sol[w[5], dU] // RE // ExpandAll
```

$$dS == \frac{dH}{T} - \frac{dP\ V[T]}{T}$$

Recall w[2]

```
w[8] = w[7] /. Sol[w[2], dH] // ExpandAll
```

$$dS == -\frac{dP\ V[T]}{T} + \frac{dT\ H^{(0,1)}[P,\ T]}{T} + \frac{dP\ H^{(1,0)}[P,\ T]}{T}$$

Also, in general,

```
w[9] = (S[P, T] /. Sol[def[dS], S[P, T]]) ==
    (Normal@Series[S[P, T], {P, P0, 1}, {T, T0, 1}] /.
      {Sol[def[dP], P], Sol[def[dT], T]}) // Sol[#, dS] & // RE
```

$$dS == dT\ S^{(0,1)}[P0,\ T0] + dP\ S^{(1,0)}[P0,\ T0] + dP\ dT\ S^{(1,1)}[P0,\ T0]$$

Neglect quadratic terms in the expansion

```
w[10] = w[9] /. dP dT → 0 /. {P0 → P, T0 → T}
```

$$dS == dT\ S^{(0,1)}[P,\ T] + dP\ S^{(1,0)}[P,\ T]$$

Equate coefficients of the previous expressions

```
w[11] = Coefficient[w[10]〚2〛, dT] == Coefficient[w[8]〚2〛, dT]
```

$$S^{(0,1)}[P,\ T] == \frac{H^{(0,1)}[P,\ T]}{T}$$

```
w[12] = Coefficient[w[10]〚2〛, dP] == Coefficient[w[8]〚2〛, dP]
```

$$S^{(1,0)}[P,\ T] == -\frac{V[T]}{T} + \frac{H^{(1,0)}[P,\ T]}{T}$$

to obtain relationships between the partial derivatives of S and H.

Cross differentiate to obtain Maxwell relations

```
w[13] = MapEqn[D[#, P] &, w[11]]
```

$$S^{(1,1)}[P,\ T] == \frac{H^{(1,1)}[P,\ T]}{T}$$

```
w[14] = MapEqn[D[#, T] &, w[12]]
```

$$S^{(1,1)}[P,\ T] == \frac{V[T]}{T^2} - \frac{V'[T]}{T} - \frac{H^{(1,0)}[P,\ T]}{T^2} + \frac{H^{(1,1)}[P,\ T]}{T}$$

Equate these expressions

```
w[15] = w[13] [[2]] == w[14] [[2]]
```

$$\frac{H^{(1,1)}[P, T]}{T} == \frac{V[T]}{T^2} - \frac{V'[T]}{T} - \frac{H^{(1,0)}[P, T]}{T^2} + \frac{H^{(1,1)}[P, T]}{T}$$

Finally, an expression for dHdP is obtained

```
w[16] = Sol[w[15], H^(1,0)[P, T]]
```

$$H^{(1,0)}[P, T] \to V[T] - T V'[T]$$

and

```
w[17] = w[4] /. w[16]
```

$$\mu JT == -\frac{V[T] - T V'[T]}{Cp}$$

BT express μ_{JT} in terms of the density $\rho(T)$

```
w[18] = w[17] /. V → Function[{T}, 1/ρ[T]] // ExpandAll
```

$$\mu JT == -\frac{1}{Cp \, \rho[T]} - \frac{T \, \rho'[T]}{Cp \, \rho[T]^2}$$

BT write this as

```
w[19] = μJT == HoldForm[ -1/(Cp ρ[T]^2) D[ρ[T] T, T]]
```

$$\mu JT == -\frac{\partial_T (\rho[T] \, T)}{Cp \, \rho[T]^2}$$

which is the same as the derived expression.

```
w[20] = (w[19] [[2]] // ReleaseHold) == w[18] [[2]] // Simplify

True
```

Part (d)

The enthalpy is

$$H = U(T) + PV \tag{16}$$

For an ideal gas $PV = \mathcal{N} k_B T$

Thus

$$H = H(T) \tag{17}$$

only. From above, the process satisfies

$$H_1 = H_2 \tag{18}$$

and so the temperature does not change.
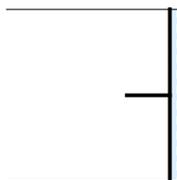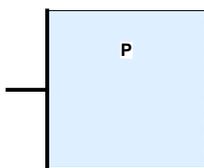
Visualization

```
Module[{L = 1, H = 2, cylinder, plug, piston, range, lab, labP, G},
 range = {{-L, L}, {-H, H}};
 cylinder = {LightBlue, Rectangle[1/2 {-L, -H}, 1/2 {L, H}], {Black,
    Line[{{-L/2, -H/2}, {L/2, -H/2}}], Line[{{-L/2, H/2}, {L/2, H/2}}] }};
 plug = {Directive[Black, Dashed], Line[{{L/2, H/2}, {L/2, -H/2}}] };
 piston = {Directive[Black, Thick],
    Line[{{-L/2, H/2}, {-L/2, -H/2}}], Line[{{-L/2 - L/4, 0}, {-L/2, 0}}] };
 labP = {Black, Text[Stl["P"], {0, H/4}]};
 lab = Stl["Fluid with mass ΔM\n is adiabatically forced\nthrough porous plug"];
 G[1] = Graphics[{cylinder, plug, piston, labP},
    Axes → None, AspectRatio → 1, PlotRange → range, PlotLabel → lab];

 cylinder = {LightBlue, Rectangle[{0.9 L/2, -H/2}, {L/2, H/2}], {Black,
    Line[{{-L/2, -H/2}, {L/2, -H/2}}], Line[{{-L/2, H/2}, {L/2, H/2}}] }};
 piston = {Directive[Black, Thick], Line[{{0.9 L/2, H/2}, {0.9 L/2, -H/2}}],
    Line[{{0.9 L/2 - L/4, 0}, {0.9 L/2, 0}}] };
 G[2] = Graphics[{cylinder, plug, piston}, Axes → None,
    AspectRatio → 1, PlotRange → range];
 Grid[{{G[1]}, {G[2]}}]]
```


**Fluid with mass ΔM
is adiabatically forced
through porous plug**

```
Module[{L = 1, H = 1/2, cylinder, plug, piston1, piston2, range, lab, labP, G},
 range = {{-L, L}, {-H, H}};
 cylinder = {LightBlue, Rectangle[{-L/2, -H}, {3 L/4, H}],
    {Black, Line[{{-L, -H}, {L, -H}}], Line[{{-L, H}, {L, H}}] }};
 plug = {Directive[Black, Thick, Dashed], Line[{{0, H}, {0, -H}}] };
 piston1 = {Directive[Black, Thick],
    Line[{{-L/2, H}, {-L/2, -H}}], Line[{{-L/2 - L/4, 0}, {-L/2, 0}}] };
 piston2 = {Directive[Black, Thick], Line[{{3 L/4, H}, {3 L/4, -H}}],
    Line[{{3 L/4, 0}, {L, 0}}] };
 labP = {Black, Text[Stl["P1"], {-L/4, H/4}], Text[Stl["P2"], {L/4, H/4}]};
 lab = Stl["Fluid is adiabatically forced through porous plug P1 > P2"];
 G[1] = Graphics[{cylinder, plug, piston1, piston2, labP},
    Axes → None, AspectRatio → 1/2, PlotLabel → lab]]
```

Fluid is adiabatically forced through porous plug P1 > P2
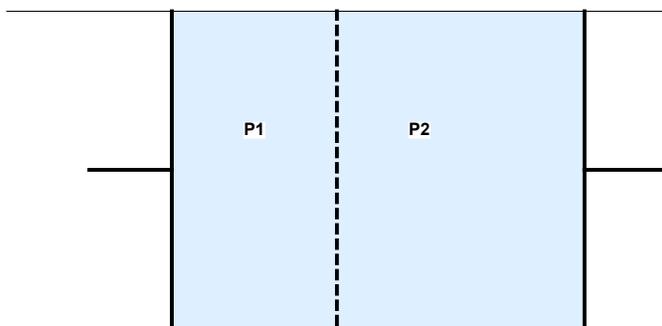
References

Informative video
https://cosmolearning.org/video-lectures/joule-thompson-throttling-adiabatic-cooling-2/

Very easy to read book on thermodynamics of fluids
https://books.google.com/books?id=8sejRP6RapMC&pg=PA211&lpg=PA211&dq=joule-thomson+flu-id+lecture&source=bl&ots=Jz5mnhkHgl&sig=kHo1OhaqA6g5NpLPghNU9bB8rBs&hl=en&sa=X&ved=0a hUKEwi30Jabp4rZAhVKzmMKHSThBD4Q6AEIVTAH#v=onepage&q=joule-thomson%20fluid%20lec-ture&f=false

nice visualization
https://chemistry.tcd.ie/staff/people/duesberg/ASIN/lecture%20notes/Chapter%204_Fugacity_+ChemPo t2011_annotated.pdf

THE JOULE-THOMPSON EXPERIMENT

A further test of intermolecular forces in real gases.
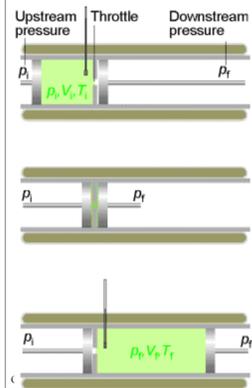
$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_P \Delta T + \left(\frac{\partial H}{\partial P}\right)_T \Delta P = 0$$

Imagine a sample of gas pushed through a porous plug, in an isolated tube (adiabatic system). The temperature is measured on each side of the plug.

Analysis

$$w = p_i V_i - p_f V_f$$

Since $\Delta U = U_f - U_i = w$ (because $q = 0$),

$$U_f + p_f V_f = U_i + p_i V_i$$
$$H_f = H_i \quad \text{i.e.} \quad \Delta H = 0$$

This is a constant enthalpy (isenthalpic) process.

What is

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad ??? = -\left(\frac{\partial H}{\partial P}\right)_T$$

Derivation of Joule-Thompson coefficient

https://cosmolearning.org/video-lectures/joule-thompson-throttling-adiabatic-cooling-2/

Useful notes on thermodynamics (Good source for derivation of Joule-Thompson coefficient)

http://www.physics.ucc.ie/apeer/PY2104/chap5.pdf