Abstract. Everything about thermodynamics. I also look at thermodynamics for engineers from a (theoretical and mathematical) physicists’ point of view. I would like to seek more cross-pollination between physicists and mathematicians and engineers in thermodynamics.

Part 1. Notes and Solutions for Thermal Physics by Ralph Baierlein

1. Background

1.1. Heating and Temperature

Heating: keep in mind 3 different types of heating for energy exchange between two systems:

1. Heating by conduction - literal contact, molecules jiggle faster from molecules jiggling faster by bouncing off them
2. Heating by radiation - em waves from hot source strike and excite target
3. Heating by convection - energy transport by flow (perhaps a fluid)

This all relates to

Q

1.2. Some dilute gas relationships.

Pressure according to kinetic theory, i.e. some kinetic theory

F ≡ force on area A due to molecules

Δp ≡ momentum transferred to wall per collision

n ≡ number of collisions in time Δt

Thus

\[ F = \frac{(Δp)n}{Δt} \]

Now Δp = 2mv \_x since Δp = mv \_x - (-mv \_x) = 2mv \_x (elastic collision with momentum conservation)
Suppose \( (v^2) = (v_1^2) + (v_2^2) + (v_3^2) = d(c_i^2) \).

An empirical gas law. Now
\[
P = \frac{N}{V} \quad \text{ (empirical)}
\]
\[
\implies \frac{P}{V} = \frac{mN}{V} = \frac{2}{\gamma}.
\]

1.3. The First Law of Thermodynamics.

Consider \( W = Q - dU \).

Consider path in \( M, \gamma: \mathbb{R} \rightarrow M = (U, V) \)
\[
\gamma(t) = (U(t), V(t))
\]
\[
\dot{\gamma} \in X(M), \gamma \big| U + V \gamma
\]
\[
W(\dot{\gamma}) = pdV(\dot{\gamma}) = pV(\dot{\gamma}) - dU(\dot{\gamma}) = Q(\dot{\gamma}) - U
\]
\[
\implies \int pV dt = \int Q(\dot{\gamma}) dt - \int U dt
\]
\[
\implies p\Delta V = \Delta Q - \Delta U
\]
p\Delta V interpreted as work done by gas. \( \Delta Q \) is heat transferred to gas system. \( -\Delta U \) is the drop in internal energy of gas system as it does work.

1.4. Heat capacity.

\[
Q = Q(\gamma, V) = \left( \frac{\partial Q}{\partial V} \right)_\gamma dV + \left( \frac{\partial Q}{\partial \gamma} \right)_V d\gamma
\]

So define \( C_V = \left( \frac{\partial Q}{\partial V} \right)_\gamma \), or interpret \( C_V \) as energy input by heating at constant volume over ensuing change in temperature.

In this case, \( \left( \frac{\partial Q}{\partial V} \right)_\gamma \).

For the case of a monatomic gas, \( U = \frac{1}{2} \gamma N, \frac{\partial U}{\partial \gamma} = \frac{N}{\gamma} \).

\[ C_V = \frac{dN}{2V} \]

\[ N \approx \text{number of molecules.} \]

Now
\[
Q = \Delta v dp + C_V d\gamma
\]
\[
Q = \Delta v dV + C_V d\gamma
\]
\[
\implies Q \wedge dp = C_V d\gamma \wedge dp
\]

Now from the thermodynamic identity, \( Q = W + dU = pdV + dU \),
\[
Q \wedge dp = pdV \wedge dp + dU \wedge dp
\]

and from (empirical) ideal gas law, \( pV = N\gamma \) (which defines a hypersurface on \( M \)),
\[
dpV + pdV = N \gamma \implies pdV \wedge dp = N \gamma \wedge dp
\]

so then
\[
Q \wedge dp = N \gamma \wedge dp + dU \wedge dp
\]

In the case of the monatomic gas, \( U = \frac{1}{2} \gamma N \), and so \( dU = \frac{1}{2} N \gamma d\gamma \) and so comparing all the equations above, one recovers
\[
C_V = N + C_V = \frac{2}{\gamma} + \frac{dN}{N}
\]

EY: 20151039 I’m curious to know how this all generalizes for \( C_V, C_P \) heat capacities, regardless of the type of molecule we consider.

The adiabatic relation for a classical ideal gas. Consider the adiabatic expansion (or contraction) of a classical ideal gas. This means that \( Q = 0 \); there is no heat exchange to or from the gas system.

Recall \( Q = dU + W \).

If \( Q = 0 \), and suppose \( W = pdV \), then \( 0 = dU + pdV \).

EY: 20151010 Either by definition, or the thermodynamic identity, \( \tau d\gamma = dU + pdV \), then \( C_V = \left( \frac{\partial Q}{\partial V} \right)_{\gamma} \). My question is this: for manifold of thermodynamic states \( M, (U, V), i.e. U \) is a global coordinate and \( V \) is a ‘local’ coordinate. One can make a Legendre transformation such that \( M \) is parametrized by \((\gamma, V), \gamma \) is the temperature. In general, one should say that \( U = U(\gamma, V) \in C^\infty(M) \), and so \( dU = \frac{\partial U}{\partial \gamma} d\gamma + \frac{\partial U}{\partial V} dV \implies dU = \Phi(M) \).

However, for this adiabatic process, we want
\[
Q = 0 = dU + W = dU + pdV = C_V d\gamma + pdV
\]

which implies that \( dU = C_V d\gamma \). What happened to the \( \frac{\partial Q}{\partial V} \)? Is it that in this adiabatic process, the internal energy of the gas system goes to either doing work (expansion) or increases due to work being done on it (contraction), and is characterized completely by a drop or increase in its temperature, respectively? And so \( dU = C_V \tau \), and \( pdV \) completely describes what’s going on with work done or work done on it.

Nevertheless, using the (empirical) ideal gas law, \( pV = N\gamma \),
\[
0 = C_V \tau + dV \implies C_V \tau + \frac{N}{\gamma} \implies \frac{dV}{\gamma} = \text{const.}
\]

Consider a path \( \gamma: \mathbb{R} \rightarrow M \), \( \gamma(t) = (\gamma(t), V(t)) \)

in \( M, \) so that \( \gamma(t) = \frac{\tau}{\gamma} + V \frac{\gamma}{\gamma} \in \mathbb{X}(M) \).

Thus,
\[
0 = C_V \frac{\tau}{\gamma} + \frac{N}{\gamma} \frac{V}{\gamma} \gamma \implies \frac{\tau}{\gamma} + \frac{N}{C_V} \frac{V}{\gamma} = \text{const.}
\]

Now
\[
\frac{N}{C_V} \frac{C_P - C_V}{C_V} = \gamma - 1
\]

which is true, assuming the (empirical) ideal gas law, the thermodynamic identity, and, surely, for the case of a monatomic gas.

Thus
\[
\tau_{V_{\gamma}^{-1}} + \tau_{V_{\gamma}^{-1}} = V_{\gamma}^{-1}
\]
A diesel engine doesn’t have a spark plug to ignite and explode the fuel. Instead, the air in the cylinder is compressed so highly that the fuel ignites spontaneously when sprayed into the cylinder.

(a) \( \tau V_f^{\gamma-1} = \frac{P_f V_f^\gamma}{P_i V_i^\gamma} = 1 \)
\( \tau_i = \left( \frac{V_i}{V_f} \right)^{\gamma-1} \tau_f \)

Run the Python script thermo.py to do the calculations. Here is (some of) the code from thermo.py for doing so (one still needs to import the necessary libraries):

```python
K = KCconv.subs(Ti, roomtempK, Prob0104ans), TF = # 1099.16054543526 F
f, 1) . subs(Vi, 15) . subs(tau)
V . subs(gamma, 1.4) . subs(K) # answer to Problem 4 of Chapter 1
```

It’s stated in Kittel and Kroemer (1980), pp. 166, Equation (37), Chapter 6: Ideal Gas, Subsection “Heat capacity” [2], that

\[ Q(\gamma) = \tau(s_f - s_i) = \frac{H_f}{N} - \frac{H_i}{N} \]

\[ L = \tau(s_f - s_i) = \frac{Q(\gamma)}{N} = \frac{N(H_f - H_i)}{N} \]

Latent heat versus heat capacity. Take slow, reversible process.

Now
\[ C_V := \frac{\partial Q}{\partial T} \]
\[ C_P := \frac{\partial Q}{\partial T} \]

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Then it’s clear that
\[ \tau \left( \frac{\partial Q}{\partial T} \right)_V = C_V \]

Now suppose \( \sigma = \sigma(\gamma, V) \).
Consider also the enthalpy, \( H = U + p V \), and so
\[ dH = dU + V dp + p dV = \tau ds + V dp \]

Now for \( \sigma = \sigma(\gamma, p) \),
\[ d\sigma = \frac{\partial \sigma}{\partial \gamma} d\gamma + \frac{\partial \sigma}{\partial p} dp = \frac{\partial \sigma}{\partial \gamma} + \frac{\partial \sigma}{\partial p} \frac{dV}{dp} \]

So
\[ C_p := \frac{\partial \sigma}{\partial \gamma} \frac{dV}{dp} = \frac{\partial H}{\partial \gamma} + \frac{\partial H}{\partial p} \frac{dV}{dp} \]

Now
\[ dH(\gamma) = dU(\gamma) + V dp(\gamma) + p dV(\gamma) = \left( \frac{\partial H}{\partial \gamma} \right)_p + \frac{dV}{dp} \left( \frac{\partial H}{\partial \gamma} \right)_p \]
so
\[ C_p := \frac{\partial \sigma}{\partial \gamma} \frac{dV}{dp} = \frac{\partial H}{\partial \gamma} + \frac{\partial H}{\partial p} \frac{dV}{dp} \]

Kittel and Kroemer (1980) [2] argues that for ideal gas,
\[ \frac{\partial H}{\partial \gamma} \frac{dV}{dp} = \frac{\partial H}{\partial p} \frac{dV}{dp} \]

since \( U = U(\gamma) \).
2.2 Conditions for coexistence. Sec. 12.3 of Baierlein (1999) [1].

Recall

\[ G = F + pV = U + pV - \tau \sigma = G(\tau, p, N) \]

Now

\[ G = G(\tau, p, N_{\text{vap}}, N_{\text{liq}}) \implies \frac{\partial G}{\partial N_{\text{vap}}} dN_{\text{vap}} + \frac{\partial G}{\partial N_{\text{liq}}} dN_{\text{liq}} = \mu_{\text{vap}} N_{\text{vap}} + 1 \mu_{\text{liq}} N_{\text{liq}} = 0 \]

\[ \implies \mu_{\text{vap}}(\tau, p) = \mu_{\text{liq}}(\tau, p) \]

From Kittel and Kroemer (1980) [2], Example: N atoms in a box, Chapter 3: “Boltzmann Distribution and Helmholtz Free Energy”, state of energy \( e_i(1) + e_i(2) + \cdots + e_i(N) \), \( \alpha, \beta, \ldots \) denote orbital indices of atoms in successive boxes, each entry occurs \( N \) times in \( Z \) (EY: 20151022) \( N \) ways to fill \( \alpha, \beta, \ldots \) with \( N \) distinguishable particles. Thus, \( Z_N = \frac{1}{N!} Z^N = \frac{1}{N!} (NqV)^N \)


4. Properties of a Pure Substance

EY: 20151030 Is the word vapor the same as gas? vapour, gaz, vapore

For coexistence equilibrium,

\[ \mu_a(p_v, \tau_v) = \mu_b(p_b, \tau_b) \quad \text{and} \quad \mu_b(p_u + d\tau, \tau_u) = \mu_b(p_b + d\tau, \tau_b + d\tau) \]

and so

\[ \frac{d\tau}{d\tau_p} = \frac{L}{N} \]

where \( \nu = \frac{\tau}{\tau_p} \), the so-called vapor pressure equation or Clausius-Clapeyron equation.

For (2) approximations, \( \Delta \tau = \tau_b - \tau_v = \frac{L}{\nu} \) and idealize vapor as ideal gas, \( p_V = N\tau \) so \( \frac{d\tau}{d\tau_p} = \frac{\tau}{\tau_p} \).

Second, if \( L \) constant,

\[ p(\tau) = p_0 \exp(-L\tau) \text{ or } \ln(p(\tau)) = -\frac{L\tau}{\tau_p} \]


Eq. 3 explains the shape of the coexistence curve between solid and gas (vapor) (sublimation) and liquid and gas (vapor) (vaporization; vaporization curve).

Saturation is this \( p = p(\tau) \) coexistence curve.

Isotherms, Isolamers

Recall \( G = F + pV \) and so \( dG = dF + Vdp + pDV = dU - \tau \sigma d\tau - \sigma d\tau + pDV = Vdp = -\sigma d\tau + Vdp \)

\[ F = U - \tau \sigma \]

\[ dG = -\sigma d\tau + Vdp \]

So then \( G = G(\tau, p) \)

\[ G = G(\tau, p, N) \]

where the latter statement is when we include particle transfer, so that

\[ dG = -\sigma d\tau + Vdp + \mu dN \text{ for } \mu = \mu(\tau, p) \]

For the ideal gas:

\[ F(\tau, V) = F = -N\tau \left( \ln \left( \frac{Nq}{V} \right) + 1 \right) \]

where

\[ n_q = \left( \frac{Nq}{V} \right)^{3/2} \]

\[ n \equiv \frac{N}{V} = \frac{p}{\tau} \]

\[ G(\tau, p, N) = -N\tau \left( \ln \left( \frac{n_q}{N} \right) + 1 \right) + N\tau = -N\tau \left( \ln \left( \frac{n_q}{N} \right) \right) = -N\tau \ln \left( \frac{Nq}{N} \right)^{3/2} \]

so then

\[ \left( \frac{\partial G}{\partial N} \right)_{\tau, p} = \mu = -\tau \ln \left( \frac{Nq}{N} \right)^{3/2} \]

For the Van der Waals gas

\[ F(\text{vdW}) = -N\tau \left( \ln \left( \frac{n_q(V - N\beta)}{N} \right) + 1 \right) \]

\[ Nq \]

\[ n_q = \frac{N}{V} \]

\[ \beta = \frac{\partial F}{\partial V} \]

\[ G(\tau, V, N) = \frac{N\tau V - N\beta}{2N_q^2} - N\tau \ln \left( \frac{n_q(V - N\beta)}{N} \right) + 1 \]

Nevertheless, consider, when considering isotherms, isolamers,

\[ dG = -\sigma d\tau + Vdp + \mu dN \]

Consider a path \( \gamma \) on constant \( \tau \), constant total number of particles \( N \), and so

\[ dG(\gamma) = Vdp(\gamma) = G_\gamma - G_\tau = \int Vdp \]

Part 3. Thermodynamics (Revisited)

5. Heat Capacity


\[ Q = \frac{\partial U}{\partial \tau} + C_V d\tau = dU + W = dU + pDV \]

Let \( c \in \Sigma \text{ s.t. } d\rho(c) = 0 \) (constant pressure). And so

\[ Q(c) = 0 + C_V d\tau(c) = \tau \sigma d\tau(c) = dU(c) + pDV(c) \]

for \( c = (\tau, 0), c = \frac{\rho}{\tau} \in T \Sigma \)

\[ C_V = \frac{\tau \sigma}{\tau_p} \ldots \frac{\partial U}{\partial \tau_p} + \frac{pDV}{\partial \tau_p} \]

for heat capacity at constant pressure is larger than \( C_V \) because additional heat must be added to perform the work needed to expand volume of gas against constant pressure.

Now recall for enthalpy

\[ H = U + pV \]

\[ H = H(\tau, p) \]
Then
\[ dH = dU + pdV + Vdp = Q + Vdp \]
Thus, for \( c \in \Sigma \), \( dp(c) = 0 \) (constant pressure). Hence
\[ dH(c) = \left( \frac{\partial H}{\partial r} \right)_p = Q(c) + Vdp = \left( \frac{\partial Q}{\partial r} \right)_p \]
Hence,
\[ C_p = \left( \frac{\partial H}{\partial \tau} \right)_p = \left( \frac{\partial Q}{\partial \tau} \right)_p \]

6. Phase Equilibrium

\begin{itemize}
  \item Phase Equilibrium
  \item Phase Diagram
  \item (Phase) Coexistence Curve
  \item Antoine Equation (parameters)
\end{itemize}

For coexistence equilibrium,\( \mu_g(p_0, \tau_0) = \mu_l(p_0, \tau_0) \) and \( \mu_g(p_0 + dp, \tau_0 + d\tau) = \mu_l(p_0 + dp, \tau_0 + d\tau) \), and so \( \frac{dp}{d\tau} = \frac{\Delta v}{\tau} \) with\( v = \frac{V}{N} \).

Make the approximation that \( \Delta v \equiv v_g - v_l \approx v_g = \frac{V}{N}g \) and idealize vapor as ideal gas, \( pV = N\tau \), so \( \frac{dp}{d\tau} = \frac{L\tau^2}{p} \).

If \( L \) constant,
\( p(\tau) = p_0 \exp \left( -\frac{L\tau}{\tau_0} \right) \) or \( \ln \left( \frac{p(\tau)}{p_0} \right) = -\frac{L\tau}{\tau_0} \).

Consider the Antoine Equation Parameters given in the NIST (National Institute of Standards and Technology) Chemistry Webbook\(^1\)
\[ \log_{10}(P) = A - \frac{B}{T + C} \]

Then
\[ P = 10^{A - \frac{B}{T + C}} = 10^A 10^{-\frac{B}{T + C}} = 10^A \exp \left( -\frac{B}{T + C} \ln 10 \right) \]

Consider how much the pressure is changed due to this \( C \) parameter. Consider \( P_0, P_1 \), defined as such:
\[ P_0 = 10^A \exp \left( -\frac{B}{T} \right), \quad P_1 = 10^A \exp \left( \frac{B}{T + C} \right) \]

So a deviation can be estimated from \( 1 - \frac{P_0}{P_1} \).

Open up \texttt{thermochem.py}. The saturation curve or coexistence curve for, for example, oxygen, from liquid to gas, can be reproduced. One needs to input in the Antoine parameters from the NIST website\(^2\).

\[ u_t(x) := u(x,t) = U(a,t) =: U_t(a) \]

\[ g(t) = g_0 \]

\[ g_t^{-1} = g_0 \]

\(^1\)Phase change data for Oxygen
\(^2\)http://webbook.nist.gov/chemistry/cgiplex.cgi?ID=C7782447&Mask=4#Thermo-Phase
References


There is a Third Edition of T. Frankel’s *The Geometry of Physics* [7], but I don’t have the funds to purchase the book (about $ 71 US dollars, with sales tax). It would be nice to have the hardcopy text to see new updates and to use for research, as the second edition allowed me to formulate fluid mechanics and elasticity in a covariant manner. Please help me out and donate at ernestyalumni.tilt.com.
7. Code listings
Demonstration using epydoc:

```bash
epydoc --pdf -o /home/fsnielsen/tmp/epydoc/ --name RBHBase wikipedia/api.py
```

This example does not use `brede_str_nmf` but another more well-documented module called `api.py` that are used to download material from Wikipedia.