Lecture 10 – Modeling liquids and solids Purdue ME 200, Thermodynamics I

Kevin J. Kircher, kircher@purdue.edu

Outline

Partial derivatives and notation

Specific heats

Modeling liquids and solids

Example

Partial derivatives

- consider a function f of two variables, x and y
- the partial derivative of f with respect to x,

$$\lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x},$$

- \diamond is the change in the output variable z = f(x, y)
- \diamond per unit change in the input variable x
- \diamond with y held constant
- in general, the partial derivative is a function of x and y

Notation for functions

- in math classes, we write z = f(x, y)
 - \diamond z denotes the variable (a number)
 - \diamond f denotes the function (a mapping from **R**² to **R**)
- in this class, we sometimes (sloppily) write

$$z = z(x, y)$$

to emphasize that z is a function only of x and y

Notation for partial derivatives

• in math classes, we write partial derivatives as

$$f_x(x,y)$$
 or $\frac{\partial f}{\partial x}$

• in this class, we write partial derivatives as

$$\left(\frac{\partial z}{\partial x}\right)_y$$

to emphasize that

- $\diamond z$ is a function of x and y only
- $\diamond~y$ is held constant when taking the derivative

Outline

Partial derivatives and notation

Specific heats

Modeling liquids and solids

Example

Specific heat at constant volume, c_v

- consider a simple compressible system in state (T, v)
- how much does its specific internal energy u(T, v) change
 - \diamond per unit change in T
 - \diamond with v held constant?
- the answer is the specific heat at constant volume,

$$c_{\nu}(T,\nu) = \left(\frac{\partial u}{\partial T}\right)_{\nu}$$

How to measure c_v ?



- we can't measure internal energy U directly
- so place system of mass *m* in rigid tank
 - $\diamond~$ no bulk motion, so $\Delta KE = \Delta PE = 0$
 - \diamond constant volume, so W=0
 - $\diamond~$ from 1st law for closed systems, $Q=\Delta U$
- add small, measured energy Q via heat transfer
- measure temperature change ΔT ; then

$$\frac{Q}{m\Delta T} = \frac{\Delta U}{m\Delta T} = \frac{\Delta u}{\Delta T} \approx \left(\frac{\partial u}{\partial T}\right)_{v} = c_{v}(T, v)$$

Specific heat at constant pressure, c_p

- consider a simple compressible system in state (T, p)
- how much does its specific enthalpy h(T, p) change
 - \diamond per unit change in T
 - \diamond with *p* held constant?
- the answer is the specific heat at constant pressure,

$$c_p(T,p) = \left(\frac{\partial h}{\partial T}\right)_p$$

How to measure c_p ?



- we can't measure enthalpy H = U + pV directly
- so place system of mass *m* in cylinder with free piston
 - $\diamond~$ no bulk motion, so $\Delta KE = \Delta PE = 0$
 - \diamond constant pressure, so $W = p\Delta V$ and $\Delta H = \Delta U + p\Delta V$
 - $\diamond~$ from 1st law for closed systems,

$$Q = \Delta U + W = \Delta U + p \Delta V = \Delta H$$

- add small, measured energy Q via heat transfer
- measure temperature change ΔT ; then

$$\frac{Q}{m\Delta T} = \frac{\Delta H}{m\Delta T} = \frac{\Delta h}{\Delta T} \approx \left(\frac{\partial h}{\partial T}\right)_p = c_p(T, p)$$

Specific heats and state transformations

• for simple compressible systems,

- $\diamond\,$ any two independent intensive properties define the state
- o it doesn't matter which two properties we choose
- \diamond for example, sometimes we choose (T, v); other times (T, p)
- equations of state, like pv = RT, allow state transformations
- for example, suppose we
 - \diamond choose state (*T*, *v*)
 - \diamond have equation of state p = f(T, v)
- then $c_p(T, p) = c_p(T, f(T, v)) =$ function of (T, v) only
- similarly, we can write $c_v(T, v)$ as a function of (T, p) only

Notes on specific heats

- specific heats are intensive properties
- they're only defined in single-phase regions
- $c_p \ge c_v$ since there's no boundary work when v is constant
- $k = c_p/c_v$ is called the specific heat ratio

Outline

Partial derivatives and notation

Specific heats

Modeling liquids and solids

Example

Approximating compressed liquids as saturated liquids

- we only have compressed liquid tables for a few substances
- for other compressed liquids, use saturated liquid properties



Moran et al., Fundamentals of Engineering Thermodynamics (2018)

Saturated liquid approximation

• for a compressed liquid in state (*T*, *p*),

 $egin{aligned} & \mathbf{v}(\mathcal{T}, \mathbf{p}) pprox \mathbf{v}_{ ext{liq}}(\mathcal{T}) \ & \mathbf{u}(\mathcal{T}, \mathbf{p}) pprox \mathbf{u}_{ ext{liq}}(\mathcal{T}) \ & \mathbf{h}(\mathcal{T}, \mathbf{p}) pprox \mathbf{u}_{ ext{liq}}(\mathcal{T}) + \mathbf{p}\mathbf{v}_{ ext{liq}}(\mathcal{T}) \end{aligned}$

• but $h_{\text{liq}}(T) = u_{\text{liq}}(T) + p_{\text{sat}}(T)v_{\text{liq}}(T)$, so

$$h(T, p) \approx [h_{\text{liq}}(T) - p_{\text{sat}}(T)v_{\text{liq}}(T)] + pv_{\text{liq}}(T)$$
$$\implies h(T, p) \approx h_{\text{liq}}(T) + \underbrace{(p - p_{\text{sat}}(T))v_{\text{liq}}(T)}_{\text{usually negligible}}$$

• so enthalpy can usually be approximated by

$$h(T,p) \approx h_{\text{liq}}(T)$$

The incompressible substance model

- $\bullet\,$ most liquids and solids are $\sim incompressible:$
 - $\diamond v$ is \sim constant
 - \diamond u ~depends on *T* only
- for incompressible substances, specific heats are equal:

$$c_{\nu}(T) = \left(\frac{\partial}{\partial T}u(T)\right)_{\nu} = \frac{du}{dT}$$
$$c_{\rho}(T) = \left(\frac{\partial}{\partial T}(u(T) + \rho\nu)\right)_{\rho} = \frac{du}{dT} = c_{\nu}(T)$$

• so we can write the (one and only) specific heat as c(T)

 Δu and Δh for incompressible substances

• from the fundamental theorem of calculus,

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} \frac{\mathrm{d}u}{\mathrm{d}T} \mathrm{d}T$$
$$= \int_{T_1}^{T_2} c(T) \mathrm{d}T$$

• also,
$$\Delta h = h_2 - h_1 = u_2 + p_2 v - (u_1 + p_1 v)$$
, so

$$\Delta h = \Delta u + v \Delta p$$

• if c is approximately constant with respect to T, then

 $\Delta u \approx c \Delta T$ $\Delta h \approx c \Delta T + v \Delta p$

Summary: finding properties of liquids and solids

- 3 ways to find properties of subcooled (compressed) liquids:
 - 1. compressed liquid table
 - 2. saturated liquid approximation
 - 3. incompressible substance model
- for solids, use the incompressible substance model

Outline

Partial derivatives and notation

Specific heats

Modeling liquids and solids

Example

Inside an insulated box, a 20 kg block of steel at 100 °C comes into contact with a block of copper at 4 °C. The blocks reach thermal equilibrium at 37 °C. What is the mass of the copper block? Use 0.49 and 0.39 kJ/kg/K for the specific heats of steel and copper.

Given and find

• given:

• find:

 $\diamond m_c$

Assumptions and basic equations

• assume:

 $\diamond \ \ {\sf closed} \ \ {\sf system}$

- \diamond no bulk motion ($\Delta KE_s = \Delta PE_s = \Delta KE_c = \Delta PE_c = 0$)
- $\diamond~$ adiabatic container (so ${\it Q}_{s}=-{\it Q}_{c})$
- o incompressible substances, constant specific heats

$$\blacktriangleright \Delta u_s = (T_2 - T_s)c_s$$

$$\blacktriangleright \Delta u_c = (T_2 - T_c)c_c$$

•
$$W_s = W_c = 0$$

• basic equations:

$$\Delta KE_s + \Delta PE_s + \Delta U_s = Q_s - W_s$$
$$\Delta KE_c + \Delta PE_c + \Delta U_c = Q_c - W_c$$

System diagrams



Solution

- energy balances simplify to $\Delta U_s = Q_s$ and $\Delta U_c = Q_c$
- since $Q_c = -Q_s$, we have

$$\Delta U_c = -\Delta U_s$$

• from incompressibility/constant specific heat assumptions,

$$\Delta U_s = m_s \Delta u_s = m_s (T_2 - T_s)c_s$$
$$\Delta U_c = m_c \Delta u_c = m_c (T_2 - T_c)c_c$$

• therefore,

$$m_{c} = -\frac{m_{s}(T_{2} - T_{s})c_{s}}{(T_{2} - T_{c})c_{c}}$$

= $-\frac{(20 \text{kg})(37^{\circ}\text{C} - 100^{\circ}\text{C})(0.49 \text{kJ/kg/K})}{(37^{\circ}\text{C} - 4^{\circ}\text{C})(0.39 \text{kJ/kg/K})}$
= 47.97 kg