THE EFFECT OF DISSOLVING SALTS OR GASES IN WATER SPRAYED ON A HOT SURFACE

by

Qiang Cui

A thesis submitted in conformity with the requirements for the Degree of Doctor of Philosophy
Department of Mechanical and Industrial Engineering
University of Toronto

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ABSTRACT

A study on the effect of dissolved salts and gas on droplet boiling and spray cooling was conducted. The effect of dissolved salts and gas on droplet boiling was observed on a hot stainless steel surface at temperatures ranging from 100°C to 300°C. Dissolving small amount of salts in water does not change the properties of water significantly; it may, however, have a great effect on droplet boiling. Dissolved salts reduced heat transfer in the evaporation regime since they lower the vapour pressure of water, while dissolved CO₂ enhanced the evaporation rate slightly. In the nucleate boiling regime, dissolved salts (Na₂CO₃, Na₂SO₄, MgSO₄) prevented bubble coalescence in the liquid and promoted foaming, reducing droplet evaporation time significantly. Heat transfer was enhanced by increasing salt concentration until it reached the "transition concentration". Above this limit, dissolved salts started to reduce droplet evaporation rate
since they lower the vapor pressure of water. Dissolved NaHCO₃ reduced droplet lifetimes even more than Na₂CO₃, because it decomposed when heated to produce CO₂, further augmenting bubble formation. It was also found that when a droplet impinged on a surface above the Leidenfrost temperature, dissolved CO₂ suppressed heterogeneous nucleation because CO₂ escaped from below the drop and prevented it touching substrate.

Experiments on spray cooling of a hot surface were performed with water sprays containing dissolved salts (NaCl, Na₂SO₄, MgSO₄). Dissolving salts in water significantly enhanced heat transfer in the transition and nucleate boiling regimes during spray cooling. The increase in heat transfer was observed at all mass fluxes and impact velocities as well as concentrations in the range of experiments conducted. The critical heat flux was found to increase with increasing molar concentration of dissolved salts in water until the concentration reached the "transition concentration". Dissolving salts in water over the transition concentrations reduced spray cooling due to the reduction of vapor pressure. Precipitated salt particles on the hot surface increased surface roughness, improving heat transfer in transition boiling. Furthermore, dissolved salts increased the Leidenfrost temperature in spray cooling by preventing bubble coalescence and producing particles which increase surface roughness.
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<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$A_1$</td>
<td>constant defined in Eq. 3.12, dimensionless</td>
</tr>
<tr>
<td>$A_2$</td>
<td>constant defined in Eq. 3.12, dimensionless</td>
</tr>
<tr>
<td>$A_3$</td>
<td>constant defined in Eq. 3.12, dimensionless</td>
</tr>
<tr>
<td>$B$</td>
<td>retarded van der Waals coefficient</td>
</tr>
<tr>
<td>$c$</td>
<td>concentration of salt, mol/L</td>
</tr>
<tr>
<td>$c_i$</td>
<td>molar concentration of ionic species $i$, mol/L</td>
</tr>
<tr>
<td>$c_t$</td>
<td>transition salt concentration, mol/L</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat, J/kg$^{\circ}$C</td>
</tr>
<tr>
<td>$d_0$</td>
<td>initial droplet diameter, m</td>
</tr>
<tr>
<td>$d_o$</td>
<td>orifice diameter, m</td>
</tr>
<tr>
<td>$d_{05}$</td>
<td>mass median diameter, m</td>
</tr>
<tr>
<td>$d_{12}$</td>
<td>Sauter mean diameter (SMD), m</td>
</tr>
<tr>
<td>$D$</td>
<td>droplet diameter, m</td>
</tr>
<tr>
<td>$D_d$</td>
<td>droplet contact diameter, m</td>
</tr>
<tr>
<td>$D_b$</td>
<td>bubble diameter, m</td>
</tr>
<tr>
<td>$g$</td>
<td>acceleration due to gravity, m/s$^2$</td>
</tr>
<tr>
<td>$H$</td>
<td>height of a droplet, m</td>
</tr>
<tr>
<td>$h$</td>
<td>film thickness between coalescing bubbles, cm</td>
</tr>
<tr>
<td>$h_0$</td>
<td>initial film thickness between coalescing bubbles, cm</td>
</tr>
<tr>
<td>$h_{lg}$</td>
<td>latent heat of evaporation, J/kg</td>
</tr>
<tr>
<td>$I$</td>
<td>ionic strength; mol/kg or mol/L</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity, W/m</td>
</tr>
<tr>
<td>$m_t$</td>
<td>spray mass flux, kg/m$^2$s</td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure in the film between coalescing bubbles, atm</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>pressure difference between upstream and downstream of a nozzle, N/m$^2$</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$Q_w$</td>
<td>surface heat flux, W/m$^2$</td>
</tr>
<tr>
<td>$Q''$</td>
<td>volumetric spray flux, m$^3$/s</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of film between coalescing bubbles, cm</td>
</tr>
<tr>
<td>$R_g$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$Re_{do}$</td>
<td>Reynold number at the orifice of nozzle</td>
</tr>
<tr>
<td>$r_b$</td>
<td>bubble radius, cm</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of the liquid film between coalescing bubbles, cm</td>
</tr>
</tbody>
</table>
$t$  
  time, s

$t^*$  
  dimensionless time

$T_a$  
  ambient temperature, °C

$T_{DNB}$  
  departure from nucleate boiling temperature, °C

$T_{Leid}$  
  Leidenfrost temperature, °C

$T_{max}$  
  surface temperature at the critical heat flux

$T_w$  
  surface temperature, °C

$U$  
  droplet impact velocity, m/s

$U_m$  
  mean droplet impact velocity, m/s

$U_o$  
  upstream velocity of the nozzle and relative velocity of the droplet to the test surface, m/s; initial droplet velocity, m/s

$\nu$  
  velocity of liquid between coalescing bubbles, cm/s

$V_d$  
  droplet volume, m$^3$

$V_b$  
  bubble volume, m$^3$

$W$  
  measured weight of a droplet, kg

$We$  
  Weber number

$We_{do}$  
  Weber number at the orifice of nozzle

$z$  
  coordinate

$Z_i$  
  charge number of ionic species $i$

**Greek Symbols**

$\theta$  
  liquid-solid contact angle, °

$\mu$  
  absolute viscosity, kg/s·m

$\nu$  
  number of ions formed upon dissociation

$\rho$  
  density, g/cm$^3$

$\sigma$  
  surface tension, g/s$^2$ or mN/m

$\lambda$  
  dimensionless film thickness, $h/h_o$

**Subscripts**

$a$  
  ambient fluid (air or vapor)

$f$  
  liquid

$g$  
  gas

$r$  
  radial

$s$  
  solid; surface

$v$  
  vapor

$w$  
  solid surface
1. INTRODUCTION

1.1 Background

Extremely high heat fluxes, in excess of $10^7$ W/m$^2$, can be dissipated when a surface is impacted by a spray of liquid droplets. While techniques such as jet impingement have shown a capacity for dissipating high heat fluxes, they produce very uneven cooling because of the large spatial variations in heat flux between the impingement zone and surrounding surface. Unlike jet impingement, spray boiling usually provides much more uniform heat transfer over the surface and is therefore widely used in industries. A spray consists of a dispersion of fine drops formed by either supplying liquid at high pressure through a small orifice (plain orifice spray) or by assisting liquid breakup with a high pressure supply of air (atomized spray). Liquid breakup results in a drastic increase in particle (drop) interfacial area to volume ratio and enhances heat transfer. Therefore, droplet cooling provides significantly higher heat fluxes than conventional alternatives such as pool boiling, and these high liquid-solid heat transfer rates allow the size, cost and complexity of equipment to be reduced. Sprays have been employed effectively to cool hot subjects in many industrial processes. Applications of sprays include evaporation of fuel droplets in metallurgy, microelectronics, nuclear plant safety, aerospace engineering, and fire fighting.

In the metallurgical industry, sprays can be used to cool a preheated metallic surface in a continuous casting process, in which uniform and rapid cooling is essential for obtaining good mechanical properties such as the strength and hardness. Slow quenching may have disastrous consequences in heat treating, as it may allow massive precipitation of the alloy solutes along grain boundaries instead of dispersing them within
the grains. In addition, spray cooling provides much more precise control of the heat transfer rate over the surface than immersion quenching by adjusting the volumetric flux or other spray parameters. Spray cooling is also used in electronic cooling processes, which demand both enhanced heat removal rates and good surface temperature control.

When quenched by a spray of water, the heat transfer from a solid surface is similar to that in pool boiling despite drastic differences in the liquid-solid contact pattern between the two cases (Toda, 1974). A hot surface during spray cooling experiences four heat transfer regimes: film boiling, transition boiling, nucleate boiling, and single-phase cooling. The surface temperature is the most important parameter in spray cooling and is used to define the four distinct heat transfer regimes of the boiling curve shown in Figure 1.1, in which heat flux is plotted as a function of the surface temperature. The corresponding temperature-time curve is shown in Figure 1.2, which displays the cooling history for the surface and exhibits the four heat transfer regimes identified on the boiling curve.

The liquid-solid contact pattern formed during spraying and corresponding heat transfer are different in each of the four heat transfer regimes. When the surface temperature initially exceeds the Leidenfrost temperature, spray cooling commences at a relatively slow rate with film boiling. In the film boiling regime, the surface is separated from the liquid droplets by a continuous thin vapor blanket developed upon droplet impact (of the order of few milliseconds). Heat transfer persists in the film boiling regime until the surface temperature drops below a limit commonly referred to as the minimum heat flux or Leidenfrost point (LFP). Below this temperature limit, heat transfer enters the transition regime, in which the droplets start to partially wet the surface resulting in a rapid increase in surface heat flux and a faster decrease in surface temperature. As the surface temperature decreases from the LFP, the heat transfer rate increases because of more efficient surface wetting and boiling on the surface until it reaches a maximum,
Figure 1.1  Boiling curve for pool boiling (Incopera, F. P. and DeWitt, D. P., 1996)
Figure 1.2  Cooling curve (Bernardin et al., 1997)
known as the critical heat flux (CHF). The critical heat flux point corresponds to the inflection point or the steepest portion of the cooling curve (see Figure 1.2). Below the critical heat flux point exists the nucleate boiling regime, where bubble nucleation is the dominant mode of heat transfer. In the nucleate boiling regime, the heat transfer rate decreases as the surface temperature decreases and bubble nucleation becomes less active. The lower boundary of the nucleate boiling regime is governed by the minimum surface superheat required for vapor bubble nucleation and bubble growth in the liquid film covering the surface. Below this surface temperature, heat transfer enters the single-phase cooling regime or film evaporation regime, in which heat from the surface is conducted through the liquid film and dissipated by evaporation at the liquid-air interface, resulting in a relatively slow cooling rate (see Fig. 1.1). This regime can exist even at a temperature several degrees above the liquid saturation temperature, depending on the surface roughness, surface material, liquid properties, and droplet parameters (velocity and droplet size).

The heat transfer associated with spray cooling involves three mechanisms: droplet-wall impacting heat transfer, air convective heat transfer, and thermal radiative heat transfer. When the surface temperature is not extremely high, radiative heat transfer is negligible. The air convective heat transfer consists of convection due to bulk air flow and local turbulent convection induced by the presence of droplets in the air. While the convective heat transfer is complicated, it is small relative to the droplet impact heat transfer. Therefore, the heat transfer in spray cooling is mainly determined by the droplet impact heat transfer, which is dependent on the impact dynamics of the droplets. Knowledge of the behavior of individual droplets impact and evaporation on hot surfaces is essential to the prediction of spray cooling heat transfer and the design of the spray cooling equipment.
When droplets travel through air to strike the hot surface, the droplet impact behavior is mainly governed by the initial droplet kinetic energy. After impacting on the surface, the droplet will overcome the surface tension force so that it spreads out. Droplet impact can be characterized by the Weber number, We, which is defined as the ratio of droplet inertia forces to surface tension forces \((\text{We} = \frac{\rho l_0^2 d_0}{\sigma})\). While droplet impact dynamics affect heat transfer between the surface and impinging droplets, heat transfer may also affect droplet impact. When droplets approach a surface at very high temperature, they evaporate, producing vapor. As a droplet moves towards the surface, the vapor pressure between the surface and the impacting droplet may offset the droplet momentum, pushing the droplet away from the surface. Consequently the dynamics of the droplet impact at high surface temperature is different from that at low temperature.

While the droplet Weber number greatly affects the droplet dynamics and heat transfer, other properties of the liquid, such as the liquid-solid contact angle and bubble density, also have substantial influence on droplet heat transfer. The liquid-solid contact angle, which determines droplet surface wetting, plays an important role in droplet dynamics and heat transfer. Low contact angle allows the liquid to generate bubbles easily, resulting in higher nucleation rate. Droplets spread out more on the surface, producing a greater contact area between the liquid and surface. In particular, surface wetting can be enhanced by dissolving surfactants in spray water to reduce the liquid-solid contact angle. Besides the effect of contact angle, nucleation sources and bubble coalescence are also important in droplet boiling. Dissolving gases in the liquid is known to enhance pooling boiling by increasing the nucleation density (You et. al., 1995). Generally, droplet heat transfer can be altered not only by changing the droplet dynamics but also by dissolving additives in the spray water to change droplet properties. To date, many researchers have examined the effect of these additives on pool boiling, however, no study has been done to investigate the effect of the dissolved gases and salts on droplet
boiling and spray cooling (Pike et al., 1955, Torikai et al., 1970, Muller-Steinhagen et al., 1987).

An extensive reviews of the literature on droplet impact dynamics and spray cooling has been compiled by Bernardin et al. (1997b). In the next section, the literature on heat transfer associated with the droplet impinging process and spray cooling will be briefly reviewed, with particular attention to studies on the effects of dissolved gases and salts on droplet boiling and spray cooling.

1.2 Literature Review

1.2.1 Heat Transfer During Single Droplet Impact

The study on droplet heat transfer began with the observation of sessile droplets in film boiling. A German medical doctor, J.G. Leidenfrost (1756) first observed that a droplet levitated above a surface once the surface was hot enough. The study of the Leidenfrost phenomenon was continued by many researchers during the nineteenth century. However, most of these studies performed on droplet boiling were empirical in nature and only focused on sessile (stationary) droplets, which exhibit different behavior from impinging droplets. In the 1950's, widespread application of spray cooling motivated research into understanding the mechanism of droplet boiling. Tamura and Tansawa (1959) first systematically investigated droplet evaporation by plotting a boiling curve of the evaporation time versus the surface temperature. They found that the boiling curve of a sessile droplet was very similar to that found for pool boiling. Droplet evaporation can be categorized into four regimes: evaporation, nucleate boiling, transition boiling, and film boiling. From then on, many experimental and numerical studies have been done on droplet impact and modelling of the heat transfer between a droplet and
surface. These studies concentrated on three groups of parameters which influence the droplet heat transfer effectiveness. The three groups are: the variables related to the droplet (subcooling, size, impact velocity, impact direction, and thermal properties); the variables related to the solid surface (shape and dimension, surface condition, and thermal properties); and the variables related to ambient conditions (ambient air/gas pressure and temperature, earth gravity).

Due to limitations of the experimental instrumentation, studies on droplet heat transfer started with the film boiling regime and then moved on to other regimes since droplets were relatively stable once levitated over a surface. Gorton (1953) found experimentally that the thickness of the water vapor layer separating a liquid droplet from the surface during film boiling increased and heat transfer decreased with surface temperature. An analytical approach was presented by Wachters et al. in 1966 to predict the thickness of this vapor layer. Baumeister et al. (1966) developed a generalized correlation of the vaporization time of a droplet in film boiling on a flat surface.

Following these studies on film boiling, numerous research studies were also conducted to investigate heat transfer in other regimes. McGinnis and Holman (1968) measured the heat transfer per drop landing on a hot surface and correlated this in terms of variables related to the liquid droplets. Pederson (1970) studied the heat transfer during impact on a heated surface of water droplets with diameters ranging from 200 to 400\(\mu\)m and approach velocities from 2.4 to 10.0 m/s. The author showed that heat transfer increased with droplet impact velocity and surface temperature had little effect on heat transfer in the film boiling regime. In this study, a definition of the heat transfer effectiveness was first introduced, which was defined as the ratio of the actual heat transfer due to the effect of the impinging droplets to the total heat transfer required for complete evaporation of the liquid droplets. Michiyoshi and Makino (1978) reported that the boiling curve in the nucleate boiling regime was a straight line parallel to the pool
boiling curve for a thin water film, no matter what material was used for the heated surface and no matter what surface conditions were manufactured. Makino and Michiyoshi (1979) continued this study to investigate the effects of the initial size of water droplets on the evaporation on heated surfaces. Bolle and Moreau (1982) found that the heat transfer effectiveness varied as the inverse of the square root of droplet diameter. Their findings were later confirmed by Labeish (1994) and Inada and Yang (1993). However, Shi et al. (1993) observed an increase in heat transfer effectiveness with velocity below 350°C, but detected a decrease above the wetting temperature. Chandra and Avedisian (1992) revealed that no transition from nucleate boiling to film boiling was observed on a porous surface at a surface temperature of 200°C, unlike that seen with a stainless steel surface. Inada and Yang (1993) conducted an experimental study on the mechanisms of miniaturization of sessile drops impinging on a heated surface at the temperatures in the range corresponding to the transition boiling regime. The effect of gravity on droplet boiling was investigated by Qiao and Chandra (1995), who reported that nucleate boiling of droplets was not affected by a reduction in gravity but that droplets could not be maintained in stable film boiling since the pressure of vapor under droplets pushed them away from the surface.

These studies on heat transfer provided fundamental insights into droplet boiling. However, complete modeling of heat transfer in spray cooling process requires better understanding of droplet impact dynamics. Observation of the impact is generally accomplished using high speed photography techniques. Savic (1958) observed the behavior of droplet impact with the aid of high speed cine photography and attributed the breakup of the droplets during impact on a very hot surface to vapor bubbles penetrating the upper free surface of the droplets. Wacheters and Westerling (1966) successfully investigated the impact and breakup of droplets striking a horizontal surface at 400°C using a single-shot flash photographic technique. Their observations were confirmed later
by the findings of Bolle and Moreau (1976), who investigated variation in the impact behavior of droplets with varying Weber number striking a surface at temperatures up to 1200°C with the aid of high-speed film-based photography (7000 frames/s). Akao et al. (1980) found that the criteria for classifying the droplet impact behavior for water in the terms of Weber number also applied to other liquids (ethanol and acetic acid). Chandra and Avedisian (1991) investigated the impact behavior of n-heptane droplets with We=43 impinging on a polished stainless steel surface at temperatures ranging from 24 to 250°C with the aid of a single-shot photographic technique. They observed the droplet spreading behavior, bubble formation, and measured transient contact angle during spreading. In a fairly recent comprehensive study, Bernardin et al. (1997) built a complete picture of the impact behavior of water drops impinging on a polished surface using both still and high-speed photographic techniques.

1.2.2 Spray cooling of hot surfaces

The widespread application of sprays has motivated research with the goal of predicting heat transfer in spray cooling. Mizikar (1970) investigated the parameters which influence heat transfer in spray cooling using commercial full cone nozzles. These parameters include spray mass flux, mean drop diameter, drop velocity, angle of impingement and wetting. Mass flux was found to have a strong relationship to the heat transfer. Hoogendoorn and den Hond (1974) studied impacting water spray heat transfer in the film boiling regime. They reported that droplet size and impacting velocity did not have any significant effect on the overall heat transfer. Bolle and Moureau (1982) also studied film boiling heat transfer of water sprays impacting downward or upward on a horizontal hot plate. Heat transfer correlations at various liquid mass fluxes were obtained.
Although these studies provided information on impacting spray heat transfer, the results could not be generalized. This is because each study was performed with specific combinations of droplet size spectrum, velocity and liquid flux. Mudawar and Valentine (1989) developed heat transfer correlations for the transition, nucleate, and single-phase regions using an electrically heated calorimeter bar exposed at one end to the spray. Although these correlations were presented as functions of local hydrodynamic distributions of the spray, they were confirmed later by Deiters and Mudawar (1990) to be applicable to all types of sprays (e.g., full cone, hollow cone, flat). Klinzing et al. (1992) extended the studies to the film and transition boiling regimes. In their study, droplet diameter was found to have a weak effect on heat transfer in film boiling for all the conditions tested. Sprays were classified into two regimes with respect to volumetric flux ($Q''$): low flux sprays ($Q'' < 3.5 \text{ kg/m}^2\text{s}$), and high flux sprays ($Q'' > 3.5 \text{ kg/m}^2\text{s}$). While mass flux had a significant influence on film boiling in both regimes, drop velocity was important only for high flux sprays. Most of the experimental studies mentioned above focused on relatively low mass flow rates less than 2 kg/m$^2$s. Ciofalo et al. (1999) conducted an experimental study on spray cooling of hot walls with mass fluxes from 8 to 80 kg/m$^2$s, mean droplet velocities from 13 to 28 m/s, and mean droplet diameter from 0.4 to 2.2 mm. The single-phase heat transfer coefficient and the maximum heat flux were found to be dependent upon the mass flux and the droplet velocity, while the droplet size had a negligible independent influence.

Pais et al. (1992) assessed the effect of surface roughness on heat transfer in spray cooling. In spray cooling of a heated surface, variations in the surface texture were found to influence the flow field, altering the maximum liquid film thickness, the bubble diameter, vapor entrapment, bubble departure characteristics, and the ability to transfer heat. The authors revealed that the maximum heat flux increased with the decreasing surface roughness. The changes in surface roughness associated with spray quenching
were also studied experimentally and statistically by Bernardin et al. (1996). Pitting and other small scale roughness features up to about 25 μm increased the bubble nucleation density during the transition and nucleate boiling regimes, while blisters and other large roughness features on the order of a droplet size (25 to 100 μm) influenced the impact and spreading of the spray droplets and, consequently, the Leidenfrost temperature.

Choi and Yao (1987) investigated film boiling heat transfer to a horizontally impacting spray. The authors reported that heat transfer was mainly controlled by the liquid mass flux. This study was extended by Yao and Choi (1987) to test the film boiling heat transfer of vertically impacting sprays. The surface orientation was found to play an important role in heat transfer. The film boiling heat flux in the vertically downward impacting spray was always higher than that in the corresponding horizontally impacting spray. This increase was attributed to secondary impactions due to rebounding droplets. This was confirmed by the findings of Groendes and Mesler (1982), who reported that the vertically impacting spray had about 1.5 times greater effectiveness, in terms of liquid evaporation, than the horizontally impacting spray. While the surface orientation was found to affect the heat transfer in these studies significantly, this effect was not obtained in a recent study (Qiao and Chandra, 1998). Qiao and Chandra (1998) assessed the effect of the surface orientation by spray cooling of a surface held in three different orientations: horizontal facing up; vertical; and horizontal facing down. No significant difference in heat transfer was observed between the three cases. They believed that the results were caused by the difference in the operation conditions. Since the test surface was smaller and the droplet impacting velocities were much higher than those used by Choi and Yao (1987), most of the impacting droplets rebound off the test surface, resulting in very few secondary impactions.

1.2.3 Effect of Dissolved Gases on Boiling
Dissolved gases are known to influence boiling heat transfer. McAdams et al. (1949) first investigated the effect of dissolved air on forced-convection, subcooled nucleate boiling of water. A strong enhancement of the boiling curve at the lower heat fluxes (partially developed nucleate boiling) was observed when air was introduced. However, the dissolved gas effect was weak in single-phase heat transfer and in fully developed nucleate boiling. Similar observations for pool boiling were made by Pike et al. (1955) from experiments with boiling on a nickel wire in water and by Behar et al. (1966) for boiling on a stainless steel tube in metaaterphenyl. Torikai et. al. (1970) measured the incipient wall superheat using platinum wires immersed in water under reduced pressure conditions (0.05 to 1.0 bar), showing a decrease in superheat with increased dissolved air content. Murphy and Bergles (1972) reported decreased wall superheat at incipience and enhanced heat transfer coefficients during low-heat-flux flow boiling when a stainless steel tube was heated in R-113 saturated with air.

Gas bubbles were found (Lorenz et. al., 1974) to initiate nucleation in the liquid. This effect was confirmed by the findings of Young and Hummel (1964), who observed heat transfer enhancement by adding spots of Teflon either on the heated surface or in pits on the surface. They attributed the enhancement to the gas or vapor trapped and held in crevices of the Teflon coating. Nucleation was initiated by the presence of the trapped gas at very low superheat levels. Since there was an abundance of available sites, the number of active sites increased rapidly as the superheat increased. The observation that entrapped gas in surface cavities facilitated the initial nucleation process was also confirmed by the experiments in which steps were taken to eliminate entrapped gas in the cavities (e.g. Kosky, 1968). In the experiments, the system was pressurized prior to heating to increase the solubility of gases in the liquid and to drive liquid into crevices in the surface, thereby eliminating most of the cavities as nucleation sites. When this was
done the superheat required to initiate nucleation was found to be of the same order as that required for homogeneous nucleation.

More recently, You et al. (1995) presented the effects of dissolved gas content on pool boiling heat transfer from a horizontal cylinder in an electronic cooling fluid (FC-72). They observed that the dissolved gas liberated from the fluid in the vicinity of the heating element during boiling enhanced pool boiling heat transfer. The authors discussed the effects of dissolved gas on boiling incipience by considering a surface cavity (shown in Figure 1.3), which had an existing nucleus containing vapor and non-condensable gas. The effective embryonic bubble size, $r_b$, under gas-saturated pool boiling was calculated using a force balance:

$$\Delta P = P_b - P_l = (P_{vb} + P_{gb}) - (P_v + P_g) = \frac{2\sigma(T_w)}{r_b}$$

where $P_{vb} = P_{sat}(T_w)$ and $P_v = P_{sat}(T_b)$

![Figure 1.3](image)

**Figure 1.3** Local and bulk thermodynamics states for a gassy saturated liquid
The pressures, $P_b$ and $P_g$ indicate, respectively, the gas partial pressure, within the bubble and within the vapor/gas mixture over the flat interface above the bulk liquid. Assuming Henry’s law to be valid for the moderate pressures investigated, the partial pressure of the dissolved gas in the bubbles was determined in terms of the liquid temperature: $P_g = xH(T_w)$. The presence of dissolved gases may reduce $P_v$, and, thus, reduce the incipient superheat value for the same critical bubble radius, $r_b$, under the same total pressure, $P_t = P_v + P_g$. Although the dissolved gas was proved to promote bubble nucleation, detailed measurements on the effect of dissolved air content in FC-72 on incipience showed that only when the dissolved gas content became high (>0.005 moles/mole) would the dissolved air have an effect on boiling. This behavior was attributed (You et al., 1990) to a locally degassed fluid layer very near the boiling sites, in which the gas was convected away from the heated wall via departing bubbles during boiling. For low-to-moderate concentrations, a larger superheat was required to initiate boiling and a hysteresis was observed between boiling curves taken with increasing and decreasing heat flux steps.

The influence of the dissolved gases (He, N$_2$, Ar, CO$_2$, C$_3$H$_8$) on boiling was also observed by Muller-Steinhagen et al. (1987) for flow of water and of n-heptane in an annulus with a heated core. It was found that the heat transfer coefficients were always increased by the presence of dissolved gases relative to the case without dissolved gases. The extent of the increase depended on the solubility of the given gas in the given liquid and could be as much as several hundred percent. Carbon dioxide, which has the highest solubility in water, was found to produce the biggest enhancement of heat transfer. In addition, the wall superheat required for the inception of bubble formation was reduced considerably to far below the saturation temperature of the pure liquid. In all these studies, the enhancement of heat transfer was not attributed to the reduction of surface tension. This was confirmed by Lubetkin et al. (1996). They designed and built an
apparatus to allow the measurement on both contact angle and surface tension under pressure. The surface tension of water was found to change from about 72 mN/m to about 57 mN/m as the presence of CO$_2$ was increased from 1 to 11 bar absolute. Therefore, the presence of dissolved gases did not change the surface tension of water at normal pressures.

Jeschar et al. (1996) studied the influence of dissolved gas in cooling water on heat transfer during immersion quenching of a hot metal surface. It was found that high concentrations of dissolved gases yielded stable vapor films, leading to low Leidenfrost temperatures. In this study, salts were dissolved in the cooling water to control the concentration of dissolved carbon dioxide. Salts displaced the dissolved gases from the water, increasing the Leidenfrost temperature. The higher the salt concentration, the lower the gas concentration thereby increasing the Leidenfrost temperature. If the salt concentrations were high enough to reduce the gas concentration to a minimum, or the cooling water was degassed, the vapor film fell apart just after immersion. While the dissolved gases affected the heat transfer in this case, the exact effect of the dissolved gases on heat transfer was not completely understood since the dissolved salts may also influenced the quenching process. Tinker et al. (1995) assessed the effect of dissolved gases on dropwise evaporative cooling in the nucleate boiling regime for surface temperatures ranging from 110°C to 180°C. Their results also found that the effect of the dissolved gases was to enhance the heat transfer for small surface temperature drops, however, the effect was small for large surface temperature drops.

1.2.4 Effect of Dissolved Salts on Boiling

Dissolved salts in the liquid may have different effects on the heat transfer, depending on the heat transfer mode. Ranz and Marshall (1952) were the first to study
evaporation of an aqueous salt-solution drop suspended from a fiber. Other studies were conducted by Trommelen and Crosby (1970), Tanno et al. (1988), and Taniguchi et al. (1999) to investigate the heat and mass transfer during evaporation and provide correlations to predict the evaporation rate. Salts were found in these studies to reduce the vapor pressure and thus decrease the drop evaporation rate.

While dissolved salts always reduce the droplet evaporation rate, the effect of salts on boiling heat transfer is complex and extends into many disciplines. Heat transfer to electrolyte solutions is a common engineering problem in the chemical and petrochemical industries. Nevertheless, only a few experimental investigations of heat transfer to electrolyte solutions can be found in the literature. Cryder and Gilliland (1932) reported that heat transfer coefficients were decreased by the addition of Na$_2$SO$_4$ to boiling water for heat fluxes below 50,000 W/m$^2$. Jamialahmadi et al. (1990) employed a precise pool boiling test apparatus together with video equipment to investigate the effect of dissolved CaSO$_4$ on the heat transfer coefficient. The heat transfer coefficient first sharply decreased with time to a minimum, followed by an increase to a maximum and a subsequent gradual decrease towards an asymptotic value. This behavior was attributed to the variation of nucleation sites with time. When the experiment started, the nucleation sites on the surface were few and the heat transfer was reduced by the formation of the deposits on the surface. The number of nucleation sites increased with increasing deposits. When the heat transfer coefficient decreased to a minimum, the formation of deposits started to enhance the heat transfer by increasing the nucleation sites. Finally, the thermal resistance caused by the deposits offset the increase in nucleation sites, resulting in a gradual decrease in heat transfer coefficient.

Najibi and Muller-Steinhagen (1996) performed a wide range of experiments to determine the effects of various dissolved salts on forced-convective, pool boiling, and subcooled flow boiling heat transfer. They also investigated the effect of dissolved salts
on bubble size and nucleate site density with aqueous solutions of a number of salts. It was found that different salts had different effects on boiling heat transfer, depending on the heat flux and the solubility of the salts in water. Forced convective heat transfer decreased with increasing ionic strength of the solution and this effect was more pronounced for salts whose solubility in water decreased with increasing temperature, these salts precipitated on the heater surface forming a thermal barrier.

The effect of dissolved salts on immersion quenching was investigated by Jeschar et al. in 1996 using various salts: NaCl, CaCl₂, MgCl₂, Na₂SO₄, NaHCO₃. The authors observed that all salts added led to an increase in the Leidenfrost temperature. While sodium chloride (NaCl) showed a relatively small influence, magnesium chloride (MgCl₂) showed effects even with small concentration. No reason for the difference in the effects was presented in this study.

1.2.5 Effect of Additives on Spray Cooling

The effect of additives on spray cooling has been investigated by several researchers. Qiao and Chandra (1998) examined the effect of surfactants on spray cooling by adding sodium dodecyl sulfate (SDS) to distilled water. The surfactant was observed to enhance nucleate boiling heat flux by up to 300 percent at all mass fluxes and impact velocities. They attributed the enhancement to the promotion of homogeneous vapor bubble nucleation and foaming in spray droplets by surfactants.

Salts, as another kind of additives, are known to have the similar effect of producing foaming in liquid. Addition of salts to water has been applied in fire fighting to obtain several advantages. Usually, water below 0°C will freeze, thus posing a limitation in low temperature operations. Certain additives, if selected properly, not only can suppress the freezing point of water but also can improve its fire suppression
effectiveness (Grove et al., 1962). This enhancement is essential to fire fighting since water usually is not particularly efficient in fire suppression unless it is delivered in the form of a mist, which does not penetrate through air easily. Compared with small droplets, large droplets have less resistance and can travel more easily through air. Although large droplets of water can be delivered easily, they are less effective since their surface-to-volume ratio is small. Besides the effect of the droplet size on fire fighting, the characteristics of water also limit its application in fire fighting. First, because of its low viscosity, water rapidly runs off the hot surface. Second, water's continued blanketing ability is limited. Third, water has relatively poor reflective powers. Adding salts in water may change these limitations and reduce them. In addition, the efficiency of large spray droplets may also be increased by the dissolved salts. Therefore, the large water droplets might approach the efficiency of the small mist droplets in extinguishing a flame while retaining the ability to penetrate air easily than mist droplets.

Finnerty (1995) reported that some water-based agents, if chosen properly, were much more effective than pure water when applied to fire fighting. Adding salts to water may increase the rate of fire suppression by more than 100%, allowing for reduction in the amount of extinguishing agents used for fire fighting. Thirteen salts were chosen in his experiments and their effects were thoroughly examined, however the mechanism associated with the effects of these salts was not explored. The concentration of salts in water was very high in these experiments, in the range of 5% to 60% by mass. The evaporation of solutions with high concentration of dissolved salts generated a heavy residual layer on the burning surface, isolating it from fresh air. The effects of salts on fire fighting are interrelated, so the effect of salts on nucleate boiling is unclear in this process.

As mentioned above, foaming may play an important role in heat transfer during droplet boiling and spray cooling. Foaming, as we know, is caused by prevention of
bubble coalescence. Inorganic electrolytes are known to always reduce the degree of bubble coalescence in stagnant liquids (Oolman and Blanch, 1986; Lesard and Zieminski, 1971); and in gas-liquid contactors (Marrucci and Nicodemo, 1967; Prince and Blanch, 1990). Marrucci (1969) was first to construct a theoretical analysis of bubble coalescence in a gas transfer field. A transition concentration was found to exist in this foaming process. Once the concentration of a substance in water reaches this threshold, bubble coalescence will be prohibited completely. This theory has been proven and developed in investigated gas-transfer processes of chemical engineering. However, the detailed mechanism involved in this foaming phenomenon during droplet boiling or spray cooling has not been investigated thoroughly and needs further study.

1.3 Objectives

The main objectives of the present work are:

1) to determine the effect of the dissolved gases on the boiling heat transfer of a water droplet impacting on a hot surface,

2) to examine the effect of the selected salts on the boiling heat transfer of a water droplet impacting on a hot surface,

3) to understand the effect of selected salts on spray cooling effectiveness.

To fulfil these objectives, the following experiments were carried out:

1) First, we observed the boiling of water droplets in which carbon dioxide was dissolved to the saturation concentration at the pressure of 1 bar on a hot surface. Surface temperature was varied from 100°C to 330°C, a range covering all the heat transfer regimes from single-phase evaporation to film boiling. Droplet evaporation on a stainless steel surface after impact was recorded using a video camera. Droplet impact on the surfaces at high temperatures, in which droplets were in transition or film
boiling, was photographed using a single shot photographic technique. The initial droplet diameter was held constant (2.02 mm±0.02mm). The ambient temperature and ambient pressure were kept constant at 22°C and atmospheric pressure, respectively.

2) Secondly, we performed an experimental investigation of the effect of dissolved salts on droplet boiling using the same procedures as those used in the first study. Na₂CO₃ was first chosen to test the effect of the dissolved salts. We then investigated the combined effects of the dissolved gases and salts in water by dissolving NaHCO₃ in water, since the NaHCO₃ will decompose to form CO₂ when it is heated. Based on the results obtained from these two experiments, we conducted an intensive experimental study of the effect of five dissolved salts (Na₂CO₃, NaHCO₃, NaCl, Na₂SO₄, MgSO₄) to elucidate the mechanisms associated with the boiling of droplets containing dissolved salts.

3) Finally, we conducted experiments on the spray cooling of a hot surface by water sprays in which salts were dissolved. The effect was measured by testing transient heat flux during spray cooling of a 25.4 mm diameter hot surface plated with nickel. The surface was an end of a copper cylinder, in which four thermocouples were inserted along the axis. The heat transfer was calculated by solving an inverse heat conduction problem. The surface was photographed during quenching using a 35 mm camera. The parameters covered in this study included: the dissolved salts and their concentration in water (0.06 mol/L to 0.4mol/L), spray mass flux (0.5 to 3.0 kg/m²s), droplet impact velocity (16 to 23 m/s) and mean droplet diameter (0.54 to 0.70 mm).
2. EXPERIMENTAL APPARATUS

To implement the objectives of this study, two experimental systems were setup to investigate the effect of dissolved additives on droplet boiling and spray cooling. They are the single droplet experiment system and the spray cooling experiment system.

2.1 Boiling of Single Droplets on a Hot Surface

The effects of dissolved additives on water droplet boiling were investigated by photographing droplet evaporation with different cameras and measuring lifetimes of water droplets on a hot surface. In this study, water was prepared by first purifying tap water and then dissolving salts or carbon dioxide into it.

2.1.1 Experimental Setup for Boiling of Single Droplets

The apparatus shown in Figure 2.1 was used to record the impact and boiling of a single droplet on a hot surface. It consisted of a droplet generation and delivery system, a heated test surface, and a camera. Droplets were formed by allowing water to flow from the tip of a 33-guage stainless steel needle held 50 mm above the test surface. In the tests, the needle valve mounted on the upstream of the needle was employed to successfully reduce the flow rate of water to a very low value. This adjustment produced uniform droplets. Droplets detached and fell under their own weight onto the test surface. The impact velocity of droplets was estimated from the distance between the needle tip and the test surface to be 1m/s. The diameter of pure water droplets generated from the needle tip was 2.0±0.2 mm, hence the droplets impacted onto the test surface with the
Figure 2.1  Schematic diagram of single droplet experimental apparatus
Weber number of 29. The test surface, 50.8 mm square and 6.35 mm thick, was made of stainless steel and finished with 600 grit emery cloth and metal polish (Part#1130607, Eagle One Industries, Irvine, CA.). The test surface was mounted on a copper block that housed two 125 Watts cartridge heaters (Firerod-J3A108, Waltow, St. Louis, MI). Chromel-Alumel thermocouples were used to measure surface temperature, which was held constant to within ±0.5°C by a temperature controller (CN 9000A, Omega Engineering, Inc., Stamford, CT) regulating power to the cartridge heaters. During experiments the surface was cleaned with a cotton swab soaked in distilled water after each droplet test. The droplet delivery system was cleaned using an ultrasonic cleaner (Model 2510, Branson, CT) before each different salt was tested.

The tests were done within a temperature range from 60°C to 340°C, which encompassed all the heat transfer regimes. During the experiments at temperatures above the Leidenfrost temperature, radiation from the heater block was high enough to warm the needle significantly. To isolate the needle from the radiation heat and prevent the droplets from striking the surface during heat-up, a stainless steel plate covered with insulation material, was placed well below the needle. This shield was removed from the test surface just before the droplet detached from the needle in each test.

2.1.2 Photography Techniques

Three cameras were employed in this study to photograph droplet impact and evaporation on the hot surface. Droplet impact on the hot surface was photographed using a digital camera. A video camera was used to record droplet evaporation, while a film camera was used to obtain consecutive stages of droplet evaporation.

Photographs of droplet impacts were taken using a single-shot flash photographic technique, which provides much better image quality than can be obtained using high
speed ciné cameras (Chandra and Avedisian, 1991). To capture crucial instances of the impact with high resolution, a 35 mm camera (Nikon F3) equipped with a bellows and a 105 mm zoom lens was employed. Sharp, high contrast photos were possible by using a high resolution film, TMAX 400, and a high intensity, short pulse flash. The flash with duration of 8 µs was produced using a General Radio Strobotac 1538-A stroboscope. By varying the time delay between the instant of droplet impact and the triggering of the flash, different stages of droplet impact could be photographed. The droplet detection technique used by Qiao and Chandra (1997) was used to trigger the flash.

The detection mechanism was composed of a H21A1 optical interrupter and a detector circuit. The operation of the detector was as follows. As the droplet fell from the hypodermic needle and passed through the slot of the optical interrupter placed 5 mm below the tip of the needle, it scattered the light received by the interrupter’s phototransistor and reduced the voltage of the interrupter’s collector, sending a pulse to a time delay circuit. The time delay circuit filtered and amplified the signal, sending two signals to trigger the stroboscope and camera shutter separately. The time delay from the instant the droplet passed through the beam to the time the stroboscope fired was controlled by varying the time delay circuit. The reference delay time corresponding to the commencement of droplet impact was set by trial and error.

The camera switched on upon receiving a trigger. It took 42 ms to open the shutter. Setting the camera exposure time at 1/8 s and triggering the flash during the exposure interval gave a flash delay time variable from a minimum of 42 ms to a maximum of 167 ms. Droplets took approximately 100 ms to fall from the needle tip to the test surface. Droplets were photographed up to 20 ms after the instant of impact. The illumination provided by the flash was much brighter than the ambient light, so that the film was effectively exposed only during the 8µs flash duration, even though the camera shutter was open for 1/8 s. Several photographs were taken for a single set of operating
conditions before adjusting the time delay to capture a later stage of impact. The droplet release and impact were sufficiently repeatable that the entire droplet deformation process could be reconstructed from photographs of different droplets, captured at progressively advancing stages of impact. The flash duration (8µs) was short enough to eliminate any blurring of photographs due to droplet motion, providing vital information about such details of impact such as film spreading, bubble formation, and droplet breakup.

Photographs of droplet evaporation were taken using a flash unit (Nikon F-28) and a 35 mm camera (Nikon F3) with a motordrive capable of advancing frames at the speed of 6 frames per second. The shot time was varied by a data acquisition and control system (DAC). Once the droplet detached and crossed the optical interrupter, it generated a peak to peak pulse through the time delay circuit (the delay time was set 0 ms) to the data acquisition system. Setting the flash at the speed of 1/1000s allowed the camera to take high quality photographs of droplet evaporation.

Droplet evaporation was also recorded using a CCD camera (TM-745E High Resolution CCD Shutter Camera). Droplet lifetime was measured by counting the time from droplet impact to the end of evaporation. Uncertainty in measurement of droplet lifetime was estimated to be 1/30 s depending on the recording speed of the Video Cassette Recorder. Droplet-surface contact diameter was measured by importing video images into a computer-based image analysis package (Image Analyst, Automatix Inc.), calibrated using the image of 1.6 mm diameter ball bearing. The resolution of our measurements, corresponding to the size of one video pixel, was ±0.02 mm. We measured liquid-solid contact angle variation during droplet evaporation by using image analysis software to detect the liquid–air interface at the edge of a droplet, and approximate it by a straight line. The contact angle lay between this line and the plane of the solid surface. The uncertainty in our measurement of contact angle was estimated to
Figure 2.2  Liquid-solid contact angle ($\theta$) measurement from an image of a water droplet taken by a video camera.
be ±2°. Figure 2.2 shows measurements of the contact angle and contact diameter of a
droplet evaporating on a hot surface.

2.1.3 Preparation of Test Water

The water used in our experiments was successively distilled, deionized and
degassed to minimize the presence of dissolved chemicals and gasses. Distilled water was
deionized in a NANOpure Bioresearch Deionization System (Model #D4754, Barnstead
Thermolyne Corporation) to an electrical resistivity of 18.3 MΩ-cm. The method most
frequently used to degas a liquid is to boil away 10 to 20% of the solvent under vacuum.
This method is effective, but is wasteful of liquid. In this study, degassed water was
prepared by freezing the liquid and then pumping down the container. Figure 2.3 shows
the experimental apparatus for degassing the water. A stainless steel chamber (88.9 mm
diameter and 152.4 mm height) was filled with deionized, distilled water and placed in a
Dewar flask filled with dry ice. Once the water froze the space above it was evacuated for
over an hour. The water was then allowed to melt, after which the freezing and
evacuation process was repeated two more times.

Salt solutions were prepared by dissolving the required amount of powdered salts
(99.7% pure, ACP Chemical Inc.) in distilled, degassed water at room temperature, and
then allowing the solution to stand for about 12 hours to ensure complete mixing. The
salts used in this study were: NaCl, Na₂SO₄, MgSO₄, Na₂CO₃, NaHCO₃. The salt solution
concentrations were well below their solubility limits in water. The solubility of
dissolved salts used in this study at room temperature can be found in Figure B.3 of

Dissolving salts in the water may change the surface tension. Surface tension
values can be calculated by relating the surface tension to the droplet’s weight (Adamson,
Figure 2.3  Experimental setup for dissolving CO$_2$. 
1982); during the droplet generation process, the droplet detaches from the tip of the needle once its own weight overcomes the surface tension force. The liquid film formed around the tip of the needle prior to detachment was so thin that the surface tension force was assumed to equal the droplet’s weight. The surface tension values of water droplets were determined using Tate’s law, \( W = \pi D_n \sigma \), where \( W \) is the measured weight of one droplet, \( D_n \) is the outer diameter of the needle (supplied by the manufacturer) and \( \sigma \) is the surface tension of water. Since the droplets in free fall were spherical, the weights of droplets could be calculated from measuring the droplet diameter. Our measurements of the surface tension of pure water agreed well with the data reported in the literature. Diameters of droplets falling after detachment were found to be 2.0±0.02 mm in all our experiments. There was no measurable difference between the diameter of droplets in which any of the selected salts was dissolved, from which we concluded that the salts did not significantly change surface tension. Previous measurements of the effects of these additives on the surface tension of water (International Critical Table, 1933) confirm that they have little influence at low concentration. During the experiments, the repeatability of these measurements was verified by photographing five different droplets at the same instant after detachment.

The basic setup used to study the boiling of single droplets containing dissolved gases is the same as the apparatus described for the study of salt additives, see Fig. 2.1. Once water was distilled and degassed, carbon dioxide was dissolved directly in water contained in the stainless steel vessel used for degassing water by pressurizing it with gas at 1 bar from a carbon dioxide tank for two days. The reservoir was shaken occasionally to speed up the diffusion rate of carbon dioxide into water. A Natelson microgasometer (Model #650, Scientific Industries Inc.) which adapts the classic Van Slyke (1924) manometric method, was used to determine the gas content. Detailed information is provided in Appendix C. During the measurement process, water was first transferred by
collecting water via the valve at the bottom of the container to a bottle and then measured by the Natelson microgasometer. The carbon dioxide content of water measured in these tests was typically 0.74 mm$^3$/mm$^3$ (at STP), which is close to the saturated value, 0.75 mm$^3$/mm$^3$ (at STP), reported in the literature (Fogg, et al. 1991). The diameter of the droplets containing dissolved carbon dioxide was measured using the same method as above. The diameter was found to be 2.0±0.02mm. Dissolving carbon dioxide into water did not change the surface tension of the water under the pressure of 1 atm. This measurement agreed well with the data reported by Jho et al. (1978).

2.2 Spray Cooling of a Hot Surface

Experimental techniques used for measuring heat transfer during spray cooling can be classified into two categories: steady state and transient methods. In steady state experiments, heat transfer rates are derived from a thermal balance between the (usually electric) power input into a solid body and the heat transferred to the spray. This application is usually limited by the maximum attainable power densities. Moreover, in a power-controlled system it is very difficult to maintain steady state conditions in the unstable region of the heat transfer curve (transition, or partial film boiling). Because of these limitations, steady state methods have usually been confined to investigations involving low heat transfer rates.

In transient experiments, the target is typically heated to a uniform high temperature and then rapidly cooled by the spray while the temperature histories at one or more locations within the sample are recorded. The surface heat flux and temperature can be calculated from the raw experimental data by smoothing the data and solving an inverse heat conduction problem. In the transient method large heating power is not
needed because it is not necessary to maintain a steady state condition. Therefore, this method is commonly employed in the study of spray cooling where the heat flux is high.

Transient spray cooling tests are usually conducted under the assumption that, despite the time-dependent conditions of the measurements, the relationship between wall temperature and wall heat transfer rates is the same as that observed under steady state conditions. This is justified by the fact that the time constants characterizing the impact, spreading and vaporization of an individual droplet are usually much shorter than the time constants of the overall cooling transient. In addition, previous studies (Mudawar, 1994, Qiao, 1996) show that the boiling curve associated with transient state spray cooling is identical to that determined from steady-state measurements. In the present study, the transient spray cooling method was used.

The apparatus shown in Fig. 2.4 was constructed to examine the effects of dissolved salts on spray cooling. The main components of the system setup are a water delivery system, a spray nozzle, a heat block, and a data acquisition and control system.

The water delivery system consisted of a water supply tank, a turbine pump (CT9755, Burks Pumps, Pique, OH), a check valve, a needle valve, and a tubing system. The turbine pump circulated water through the stainless steel tubing and valves to the spray nozzle. Only a portion of the total flow delivered by the pump was actually supplied to the nozzle, while the balance was bypassed through the release valve to the supply tank. The flow rate of water supplied to the nozzle was measured by a flow meter (GF1360, Gilmont Instruments, Barrington, IL). It was controlled by adjusting the pressure regulator (26 A, Watts Regulator Groups, North Andover, MA) and fine tuning a micrometer valve. The flowmeter has a resolution of 1ml/min. The nozzle inlet pressure was measured using a digital pressure gauge (OMEGA DPG-500) with an accuracy of 7kPa, which was situated just upstream of the spray nozzle. The spray hydrodynamic parameters (i.e. volumetric flow rate \(Q\), impact velocity \(U_m\)) were controlled by varying
Figure 2.4  Experimental apparatus for spray cooling
the flow rate and the nozzle pressure. After impinging upon the heated surface, the vapor generated was exhausted from the test chamber through the front, while the unevaporated liquid was collected and discharged through a drainage tube at the bottom of the test chamber.

The heat block and spray nozzle were housed in the aluminum chamber (152 mm long × 152 mm wide × 254 mm high), which was mounted on a rotation stage. The front of the chamber was open, while a clear plastic window in the rear allowed the test surface to be illuminated by a flash unit (Nikon Speedlight 5B-28).

The heat block shown in Figure 2.5 was composed of heated body, two electric heaters, and insulation wool. The test cylinder shown in Figure 2.5a was made of oxygen free copper. The surface was polished and nickel-plated to a thickness of 10μm to minimize oxidation and corrosion. The bottom of the test cylinder was bolted to a heat copper block that housed two 500W cartridge heaters (see Figure 2.5b). The test cylinder was surrounded with silicon rubber to seal and insulate the test cylinder, while the heat copper was insulated with mineral wool to reduce losses. Four 0.5 mm diameter Chromel-Alumel K-type thermocouples (KMTSS-020G-6, Omega Engineering, Inc., Stamford, CT) were inserted into holes drilled 6.35 mm apart along the axis of the heated body, with the first thermocouple positioned 0.4mm below the test surface (Figure 2.5a).

To further enhance the transient response, high thermal conductivity paste was applied during the installation of the thermocouples to ensure excellent contact between the copper and the thermocouple bead. The temperature registered at the top thermocouple was considered to be the initial surface temperature and held at 240°C (within ±1°C) by regulating the power to the heating cartridge. The heater was turned off during spray cooling. The real surface temperature during the spray cooling processes was extrapolated from measurements by thermocouples embedded beneath the surface, assuming one-dimensional heat conduction within the test surface.
4 holes with 4-40 threads, 3mm deep, equally spaced on a 9.5 mm dia circle

6 holes with 6-32 threads, equally spaced on a 38 mm dia circle

Holes for thermocouples 4 holes 0.8 mm dia

SECTION A-A

Figure 2.5a  Test cylinder dimensions and thermocouple positions
SECTION A-A

Figure 2.5b  Dimensions of the copper heater block
The spray nozzle was located normal to the test surface. Spray mass flux was measured by collecting water into a 100ml graduated cylinder through a copper tube with the same internal diameter as that of the test surface and dividing the volume of collected water by the product of the fill time and inlet area. The inlet of the collecting tube was placed at the same distance from the spray nozzle as the test surface. Uncertainty in measurement of the flow rate was estimated to be ±4%. Since the salt concentration used in the test water was so low that the density of water did not change significantly, the change in mass flux due to the additives was found to be less than the uncertainty in measurement.

In the experiments, NaCl, Na₂CO₃, NaHCO₃, Na₂SO₄, and MgSO₄ were chosen as the test salts. The effects of different dissolved salts on spray cooling were studied using 0.06 mol/L as the typical concentration, while the effects of the salt solution concentration on spray cooling was examined using MgSO₄ with varying concentrations, specifically 0.01, 0.06, 0.2, and 0.4 mol/L. Fresh salt solutions were prepared before each experiment by weighing and dissolving the selected salt into distilled water, and stirring the water in the tank with a stainless steel bar by hand for 5 minutes to keep the solution concentration uniform. The water was distilled using a distilling system (#MP-1, Barnstead Mega-Pure System) immediately prior to use to minimize the presence of dissolved gases.

The test surface was prepared by cleaning it with metal polish (Part #1130005, Eagle One Industries, Irvine, CA) and washing it first with acetone and then with distilled water before each test. The water delivery system was purged by disconnecting the supply tube downstream of the pressure regulator and pumping the water out of the reservoir to an open plastic tank for 30 s. This pumping process was conducted to reduce the effect of corrosion in the turbine pump. The tube was disconnected to prohibit the water from routing through the release valve back to the supply tank. After flushing the pump with the salt solution, the system was reconnected and the heaters were then
switched on to warm the test surface. This process was continued until the surface temperature, as measured by the uppermost thermocouple, was stable at 240°C. The pump was activated to flush the tubing system and the spray nozzle for 30 s, with a plastic plate held in front of the spray nozzle to shield the test surface. Once the nozzle pressure reached the required steady value, the heaters were turned off and the plastic plate was removed to allow the water from the nozzle to spray on the test surface directly. The test surface was cooled from 240°C to 95°C in a period of 5 s to 300 s, depending on the spray parameters. The output from the inserted thermocouples was first amplified and filtered using a 5B37 thermocouple module, and then recorded using a PCI-MIO-16E-4 board (National Instruments) in a Power Macintosh 7200/120 computer. The data acquisition system was controlled using a LabVIEW program (refer to Appendix A for details of the program).

Photographs of the spray cooling process were taken using a 35 mm film camera (Nikon F3) with Kodak TMAX 400 film and the lens aperture set to 22. The camera was triggered by the user through a SCB-68 board at specific preset surface temperatures. The signal from the uppermost thermocouple was processed using an OMNI AMP and input through the SCB-68 to the computer. The uncertainty in the measurement of temperature with the OMNI AMP was ±0.5°C. The test surface was illuminated through the rear window of the test chamber using a Nikon 5B-28 flash unit with a speed of 1/2000 s, while the rear window was covered with white paper to diffuse the incoming light. Different spray cooling regimes can be distinguished by comparing the video images with the simultaneously measured surface temperature.
3. EFFECT OF DISSOLVED SALTS ON DROPLET BOILING

3.1 Effect of Dissolved Salts on Droplet Boiling

Previous studies (Lessard and Zieminski, 1971) reported that bubble coalescence in aqueous solutions is largely inhibited above a critical concentration range of electrolyte, the so-called transition concentration. While the transition concentrations of salts are determined possibly by many factors such as ionic strength, viscosity, size of ions, they were found to be rough functions of the valence combinations of salts (Lessard and Zieminski, 1971). When two 0.36 cm diameter bubbles were brought to contact each other in a variety of electrolyte solutions, 3-1 and 2-2 electrolytes such as MgSO₄ and Al₂Cl₃ were observed to prevent coalescence in the concentration range 0.030-0.035M, 2-1 and 1-2 electrolytes such as Na₂SO₄ and MgCl₂ in the range 0.056-0.060M, and 1-1 electrolytes such as NaCl and NaBr in the range 0.16-0.23M. In this study, we attempted to apply the results obtained from these previous studies on bubble coalescence in chemical engineering to droplet boiling. So we chose one salt from each group to investigate the effect of dissolved salts on droplet boiling. The chosen salts include NaCl, Na₂SO₄, and MgSO₄. Besides the three salts, sucrose was also used as an additive in this study to distinguish the effect of ions from the effect of viscosity in that sucrose does not ionize in solution.

In order to examine the effect of salts on droplet boiling, we conducted experiments on these salt solutions in a surface temperature range from 90°C to 220°C. This temperature range encompasses all the droplet evaporation regimes: evaporation, nucleate boiling, transition boiling, film boiling. The concentration of dissolved salts in water was nominally 0.06 mol/L.
Figure 3.1 shows the evolution of droplet lifetimes with increasing surface temperature. Each data point represents the average of five measured values with error bars marking the highest and lowest measured values. When the surface was heated to 90°C, the droplets were in the evaporation region, all the dissolved salts increased the droplet lifetime by reducing the vapor pressure. Although this reduction of vapor pressure was small at the beginning, it increased as the droplet evaporated and the salt concentration increased. Increasing the surface temperature above 130°C led the droplets to be in a state of nucleate boiling. Dissolved NaCl did not have any obvious effect on the droplet boiling, however, both dissolved Na₂SO₄ and MgSO₄ reduced the droplet lifetime by 50%.

This experiment shows that dissolved salts are able to enhance boiling heat transfer of droplets significantly. To understand the mechanism associated with this improvement, we continued this study by examining boiling of droplets containing different salts deposited on a stainless steel surface at 130°C, which led to nucleate boiling in a water droplet. The lifetime of a droplet boiling on a surface at a temperature of 130°C is in the range of 3 to 12 s (see Fig 3.1), which is long enough for us to precisely investigate the effects of dissolved salts.

Figure 3.2 shows photographs of the evaporation of droplets of pure water, NaCl solution and Na₂SO₄ solution on a stainless steel surface at a temperature of 130°C. Each column in Fig. 3.2 shows successive stages during the droplet lifetime, and each row shows droplets boiling at the same time (t) measured from the instant of droplet impact on the surface, as indicated besides each row of photographs. The lower part of image shows the reflection of the droplets on the surface. By examining the video record of droplet evaporation, it was evident that a number of small bubbles nucleated inside the droplets immediately after impact, formed by cavities on the heater surface. However, these bubbles rapidly coalesced, so that by t=0.5 s (the second frame in Fig. 3.2) only one
Figure 3.1  Variation of salt solution droplet lifetime with the increasing surface temperature.
Figure 3.2 Evolution of droplets containing: a) pure water, b) NaCl (0.06M), c) Na$_2$SO$_4$ (0.06 M), once impacted on a hot surface at a temperature of 130°C.
large bubble was evident. For pure water, this bubble grew larger as the droplet evaporated, until it finally broke through the droplet surface. No more bubbles were produced in droplet; as the liquid evaporated it cooled the stainless steel substrate too much to support further nucleation. Dissolved NaCl had little effect on nucleate boiling of a droplet (Figure 3.2b). The boiling behavior of the droplet containing dissolved NaCl was very similar to that of a pure water droplet (Figure 3.2a). The bubbles that formed immediately after the droplet was deposited also coalesced quickly to form a big bubble. The big bubble grew larger until it burst. Dissolved NaCl was found to increase the droplet evaporation time slightly. This increase in evaporation time was attributed to the reduction of vapor pressure caused by the dissolved NaCl.

Dissolved Na$_2$SO$_4$ had significantly different effects on nucleate boiling from those of dissolved NaCl. Once a droplet containing dissolved Na$_2$SO$_4$ landed on the hot surface, many bubbles were produced. These bubbles did not combine very quickly, but grew larger, greatly expanding the bubble diameter (see Fig. 3.2 c). Consequently the contact area between the liquid and the hot surface was increased rapidly. The droplet lifetime was reduced to about 50% compared to that of pure water.

3.2 Effect of Dissolved Salt Concentration on Droplet Boiling

Dissolved MgSO$_4$ had an effect similar to that of Na$_2$SO$_4$. Figure 3.3 shows variation of the boiling behavior of a droplet of 0.01 M, 0.06 M, and 0.4 M solution, respectively. When the concentration was very low, the boiling behavior of a droplet was similar to that of a pure water droplet. However, when the concentration was increased to 0.06 M, the suppression of bubble coalescence became pronounced. When the concentration was increased to 0.4 M, the behavior of the bubbles was similar to that for the 0.06 M solution and the liquid-solid contact area was expanded greatly (see Fig. 3.3c).
Figure 3.3  Evolution of droplets containing: a) MgSO₄ (0.01M), b) MgSO₄ (0.06M), c) MgSO₄ (0.40 M), once impacted on a hot surface at a temperature of 130°C.
The only difference was that the droplet lifetime was found to increase slightly. We believed that this was caused by the reduction in vapor pressure. Figure 3.3 suggests that the dissolved salt concentration plays an important role in enhancing droplet boiling.

Figure 3.4 shows the lifetimes of pure water droplets and droplets containing dissolved NaCl, Na₂SO₄, MgSO₄, and sucrose with different concentrations. Both dissolved NaCl and sucrose increased the droplet lifetime (see Fig.3.4). The droplet lifetimes increased with the molar concentration in the two solutions. Dissolved Na₂SO₄ and MgSO₄ reduced the droplet lifetime slightly at low concentrations but significantly at high concentrations. Once the concentration of the dissolved salts in water reached a limit, the reduction of the droplet lifetime became almost constant; the threshold concentrations of dissolved Na₂SO₄ and MgSO₄ were 0.06 mol/L and 0.11 mol/L, respectively. If the concentration of these dissolved salts exceeded 0.3 mol/L, the droplet lifetime started to increase with the concentration.

The results shown in Fig. 3.2 and 3.3 demonstrate that bubble coalescence plays an important role in droplet boiling. Since the volume of a liquid droplet is fixed, retarding bubble coalescence expands the droplet diameter and therefore the contact area between the droplet and the hot surface, improving heat transfer. The ability of dissolved salts to prevent coalescence of vapor bubbles has been documented by many researchers (e.g. Marruci and Nicodemo, 1967; Lessard and Zieminski, 1971; Zieminski and Whitemore, 1971; Keitel and Onken, 1981; Craig et al., 1993; Pashley and Craig, 1997). The merging of two bubbles is inhibited if the liquid film between them is stabilized. Surfactants achieve this by altering the surface tension of the liquid. Qiao and Chandra (1997) demonstrated that adding a surfactant to water droplets boiling on a hot surface prevents bubble coalescence, making the liquid foam and greatly reducing evaporation time. Although adding small amount of salts to water does not change the surface tension of the
Figure 3.4 Variation of the droplet lifetime with the solution concentration once a droplet containing a) NaCl, b) Na$_2$SO$_4$, c) MgSO$_4$ impacted on a hot surface at a temperature of 130°C.
bulk liquid significantly, it does cause obvious change in local surface tension where the salt concentration is high. When two bubbles approach each other, the dissolved salt in the liquid between the two bubbles may not be able to diffuse quickly away, increasing the concentration locally and thereby making the surface tension higher which retards bubble coalescence. This is one of the possible effects of dissolved salts on bubble coalescence. In fact, inhibition of bubble coalescence may also be attributed to several other effects of dissolved salts on water. Electric charge accumulating on the surfaces of bubbles may produce a repulsive force, preventing them from approaching each other (Keitek and Onken, 1981). Dissolved salts may also change water structure and hence reduce the hydrophobic force of attraction.

3.3 Model of Bubble Coalescence in Salt Solutions

To date, a number of theories to explain the effect of dissolved salts on bubble coalescence have been proposed. However, none of them gives a full reasonable explanation of this phenomenon. The only quantitative model was initially proposed by Marrucci (1969) and then extended by other researchers (Sagert and Quinn, 1978, Oolman and Blanch, 1986, Prince and Blanch, 1990). This model only includes the effect of surface tension force on the bubble coalescence process.

Marruci (1967) noted that the efficiency of the inorganic electrolytes in inhibiting coalescence depends on the valence and the derivatives of the surface tension versus concentration curve. Marrucci (1969) developed an expression for the concentration of salt necessary to immobilize the gas-liquid interface in coalescing bubbles. Figure 3.5 shows the proposed coalescence process of two bubbles. Bubble coalescence can be considered to be a three-step process:
Figure 3.5  The assumed process of bubble coalescence (Marrucci model).
1. The bubbles come into contact with each other within the liquid phase. The bubble surfaces are flattened against each other, leaving a thin liquid film separating them. This step is controlled by the hydrodynamics of the bulk liquid phase.

2. This intervening liquid film thins to about $10^{-6}$ cm (Oolman and Blanch, 1986) before it will rupture. If this thinning mechanism takes longer than the bubble contact time, coalescence will not occur. This step is controlled by the hydrodynamics of the liquid film.

3. Once the film is sufficiently thin it will rupture via an instability mechanism. This step is very rapid in comparison to the first two.

During a bubble coalescence process, the force driving the thinning of the film includes two parts: the capillary pressure in the film and the Hamaker force which is the intermolecular attraction force. In Marucci’s model, a constant volume element of fluid between two coalescing bubbles is considered to undergo elongation. As the surface area increases, a surface tension gradient develops along the radial direction since the film salt concentration increases due to exclusion of salt from the increased surface area. Finally, a force balance between the driving force and the one caused by the surface tension gradient will develop in the film and immobilize the thinning process. Marucci’s model derives from a simple force balance, neglecting inertia terms.

Prince et al. (1990) modified the Marucci model with the basic Navier-Stokes equation (3.1) including the inertia terms. The liquid film between coalescing bubbles is taken to be a cylinder of radius $R$ and height $h$.

\[
\rho \left( \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_z}{r} \frac{\partial v_r}{\partial z} \right) = -\frac{\partial P}{\partial r} - \left( \frac{1}{r} \frac{\partial (r \tau_{rr})}{\partial r} + \frac{1}{r} \frac{\partial \tau_{r\theta}}{\partial \theta} - \frac{\tau_{r\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z} \right)
\]

(3.1)

In order to solve this equation, the following simplifying assumptions are made for the thinning process:

1) The flow of the liquid film is symmetric, so all terms with respect to $\theta$ are eliminated.
2) Plane parallel film geometry.

3) The velocity profile in the thinning film is flat, so $\partial u / \partial z$ is equal to 0.

4) The film thinning rate is independent of radial position.

5) No electric force.

Based on the above assumptions, Eq. (3.1) for an incompressible Newtonian fluid is simplified as:

$$\rho \left( \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = - \frac{\partial P}{\partial r} + \mu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( rv_r \right) \right] + \frac{\partial \tau_{rz}}{\partial z} \tag{3.2}$$

Since the velocity profile in the plane parallel film is flat, $v_r$ can be substituted by the average liquid velocity in the thin film. The average liquid phase velocity at an arbitrary radial position can be derived from a mass balance on the liquid:

$$v_r = - \frac{r}{2h} \frac{dh}{dt} \tag{3.3}$$

Considering the flat velocity profile assumption, the viscous term in Eq. (3.2) can be shown to be zero. The remaining terms in Eq. (3.2) can be integrated with respect to $z$ over the width of the film to obtain:

$$\rho \left( \frac{\partial \overline{v_r}}{\partial t} + \frac{1}{2} \frac{\partial \overline{v_r}^2}{\partial r} \right) = - \frac{\partial P}{\partial r} + \left( \tau_{r \theta} \right)^{h/2} \left( \tau_{r \theta} \right)^{-h/2} \tag{3.4}$$

where

$$\overline{v_r^{\prime \prime}} = \frac{1}{h} \int_{-h/2}^{h/2} v_r^{\prime \prime} dz \tag{3.5}$$

The shear force term in Eq. (3.4) can be simplified using a force balance on an element of the film surface:

$$\left( \tau_{r \theta} \right)^{h/2} \left( \tau_{r \theta} \right)^{-h/2} = 2 \frac{\partial \sigma}{\partial r} \tag{3.6}$$

Taking into consideration that $P$ is independent of $z$ and $\overline{v_r^2} = \overline{v_z^2}$ in the liquid film, Eq. (3.4) can be expressed as follows:

$$\rho \left( \frac{\partial \overline{v_r}}{\partial t} + \overline{v_r} \frac{\partial \overline{v_r}}{\partial r} \right) = - \frac{\partial P}{\partial r} + 2 \frac{\partial \sigma}{h \partial r} \tag{3.7}$$
Integration over the radial dimension of the film and substitution of the expression for the radial velocity yield:

\[-\frac{\rho R^2}{2h} \frac{d^2 h}{dt^2} + \frac{5\rho R^2}{8h^2} \left( \frac{dh}{dt} \right)^2 - \frac{2\Delta \sigma}{h} + \Delta P = 0 \]  \hspace{1cm} (3.8)

where \( \Delta \sigma \) can be obtained from Marrucci’s model (1969).

\[ \Delta \sigma = -\frac{1}{\nu h} \left( \frac{2c}{R_s T} \right) \left( \frac{\partial \sigma}{\partial c} \right)^2 \]  \hspace{1cm} (3.9)

and

\[ \Delta P = -\left( \frac{2\sigma}{r_b} + \frac{B}{h^4} \right) \]  \hspace{1cm} (3.10)

where \( r_b \) is the bubble diameter, \( B \) is the retarded van der Waals coefficient, \( \nu \) is the number of ions formed upon dissociation, \( R_s \) is the gas constant, and \( T \) is the temperature.

Substitution of these terms into Eq. (3.8) yields:

\[-\frac{\rho R^2}{2h} \frac{d^2 h}{dt^2} + \frac{5\rho R^2}{8h^2} \left( \frac{dh}{dt} \right)^2 + \frac{4c}{h^2 \nu R_s T} \left( \frac{\partial \sigma}{\partial c} \right)^2 - \frac{2\sigma}{r_b} + \frac{B}{h^4} = 0 \]  \hspace{1cm} (3.11)

Nondimensionalization of Eq. (3.11) gives:

\[ \frac{\partial^2 \lambda}{\partial \tau^2} = \frac{1.25}{\lambda} \left( \frac{\partial \lambda}{\partial \tau} \right)^2 - A_1 \lambda + \frac{A_2}{\lambda} - \frac{A_3}{\lambda^3} \]  \hspace{1cm} (3.12)

where

\[ \lambda = \frac{h}{h_0} \quad \tau^* = \left( \frac{\sigma}{\rho h_0} \right)^{1/2} t \]

\[ A_1 = \frac{4h_0^2}{R^2 r_b} \quad A_2 = \frac{8c h_0}{\nu R^2 R_s T} \left( \frac{\partial \sigma}{\partial c} \right)^2 \quad A_3 = \frac{2B}{h_0 R^2 \sigma} \]

The transition concentration, which causes the abrupt change in film thinning behavior, can be calculated from Eq. (3.12) as follows:

\[ c_t = 1.18 \nu \left( \frac{B \sigma}{r_b} \right)^{1/2} R_s T \left( \frac{\partial \sigma}{\partial c} \right)^{-2} \]  \hspace{1cm} (3.13)

Eq. (3.13) shows that, when vapor bubbles are brought into contact with each other in a salt solution at a specific temperature, the transition concentration is a function
of bubble size. As the radius of coalescing bubbles increases, the salt transition concentration required for prohibiting bubble coalescence decreases. The variation of the transition concentration for the three dissolved salts in this study with the bubble radius calculated from the equation (3.13) is displayed in Figure 3.6.

In droplet boiling, the bubble size in the droplets varies with wall temperature, roughness, convection, and bubble growth rate. Once small bubbles nucleate in a droplet and then coalesce to form big bubbles, these big bubbles may be prohibited from coalescing further because of the resulting bubble size. Therefore, there is no fixed bubble size that can be measured experimentally for calculating the transition concentration. In this study, the radius of bubbles in a boiling droplet was estimated to be in the range from 0.1 to 0.5 mm by measuring off photographs of droplets (see Fig. 3.2 and Fig. 3.3).

To verify the model derived above, bubble sizes \( r_b \) in boiling droplets were calculated using the experimental transition salt concentrations obtained from Fig. 3.4 and compared with the experimental values. Calculations of bubble sizes \( r_b \) were performed by rearranging Eq. (3.13) to the following form.

\[
r_b = \left(1.18v \frac{RT}{c_i}\right)^{1/2} B \sigma \left(\frac{\partial \sigma}{\partial c}\right)^{-1}
\]  

(3.14)

where surface tension gradients \( (\partial \sigma / \partial c) \) for the salts of interest at room temperature were used in the calculations, since no literature data are available at the temperature of 100°C and the variations of the gradients with temperature are negligible (Horvath, A. L., 1985). The values of retarded van der Waals coefficient \( B \) and surface tension gradients at room temperature can be found in the literature (Prince and Blanch, 1990; International Critical Tables, 1933). The calculated and experimental bubble sizes corresponding to the experimental transition concentrations are shown in Table 3.1.
Figure 3.6 Variation of the transition concentration versus the radius of coalescing bubbles in a salt solution at a temperature of 100°C.
Table 3.1 Calculated and experimental bubble sizes corresponding to the experimental transition concentrations ($c_r$)

<table>
<thead>
<tr>
<th>salt</th>
<th>$d\sigma/dc$ gcm$^2$/s$^2$mol</th>
<th>$c_r$ from experiments mol/L</th>
<th>bubble radius from Eq. 3.12 mm</th>
<th>bubble radius from experiments mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1,700</td>
<td>~</td>
<td>~</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>2,700</td>
<td>1.1</td>
<td>1.3</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>3,200</td>
<td>0.6</td>
<td>0.7</td>
<td>0.1–0.5</td>
</tr>
</tbody>
</table>

Table 3.1 shows that the calculated bubble sizes ($r_b$) are larger than what is observed. This difference is caused possibly by the assumptions made for the model, which does not consider the special conditions in boiling heat transfer. First, when a bubble produced by heat grows in the liquid, the dissolved salt will accumulate in the vicinity of the bubble, therefore, the concentration of the bulk liquid should not be used to estimate the transition concentration. Second, the electrostatic force caused by the ions accumulating at the bubble interface may prevent bubbles from coalescing. Third, the dissolved salts increase the surface tension of the liquid at the interface, and this interface with higher surface tension can cause Marangoni convection which drags the bulk liquid toward the film between the two bubbles. The current model is derived from equation (3.1), which does not include the Marangoni effect. Therefore this model can not be applied directly as such to boiling systems, distillation, etc., where Marangoni effects are present. If all these effects are taken into account in the model, it may be possible to predict the transition concentration with more accuracy.

The above model mainly attributes the effect of dissolved salts on bubble coalescence to changes in surface tension. However, we may also link this effect to the
ionic strength of solutions, which is not directly accounted for in the model. Ionic strength
(I) is defined as a function of valence, number of ions, and salt concentration in water.

\[ I = 0.5 \sum c_i Z_i^2 \]  

(3.15)

where:

\( c_i \) is the molar concentration of ionic species \( i \) (mol/L), and \( Z_i \) is the charge number of ionic species \( i \).

We compared the ionic strength in the solution with the reduction of droplet lifetime caused by the dissolved salts (Fig. 3.4). It was found that the reduction was linked to the ionic strength in the solutions. The higher the ionic strength is, the bigger the reduction is. This dependence of bubble coalescence on ionic strength was confirmed by the findings of Chang et al. (1986), who reported that increasing the ionic strength of saline solutions inhibited bubble coalescence and enhanced gas-liquid mass transfer. In fact, the effect of ionic strength is consistent with the effect of changes in surface tension. The increase of surface tension caused by addition of a strong electrolyte to water may be considered to be mainly due to the repulsion of ions from the surface by the electrostatic image force (Stairs, 1995).

Dissolved salts not only have an influence on the transition concentration but also on droplet lifetime (see Fig 3.4). Dissolved MgSO\(_4\) had a bigger effect on reducing droplet lifetime than dissolved Na\(_2\)SO\(_4\). This difference may be attributed to the reduction of the vapor pressure caused by the dissolved salts. In a droplet boiling process, vapor partial pressure is one factor that determines the bubble growth rate and therefore the expansion of the droplet. Only when the pressure inside the growing bubble is high enough to overcome the liquid-solid surface tension, can the bubbles expand the droplet size and thereby increase heat transfer. The vapor pressure of a MgSO\(_4\) solution decreases with an increase in the concentration of the solution less than that of a Na\(_2\)SO\(_4\) solution.
Dissolved NaCl increased the droplet lifetime within the concentration range from 0.0 to 0.40 mol/L (see Fig. 3.4). The boiling behavior of a droplet containing a dissolved salt is determined by three major factors; namely, vapor partial pressure, the capability of suppressing bubble coalescence, and the diffusion coefficient of the salt in water. At low concentrations, dissolved NaCl reduces the vapor partial pressure of water and has a very small effect on bubble coalescence. At moderate concentrations, the solutes accumulating at the bubble interface diffuse rapidly to the bulk liquid, because of the big difference in concentration between the interface and the bulk solution. The diffusion coefficient of NaCl in water is much higher than those of Na$_2$SO$_4$ and MgSO$_4$ (Zeytsev et al., 1992). The diffusion coefficients of the three salts in a 0.1M solution at 100°C are: 1.988×10$^{-9}$ m$^2$/s (NaCl), 1.244×10$^{-9}$ m$^2$/s (Na$_2$SO$_4$), and 0.892×10$^{-9}$ m$^2$/s (MgSO$_4$). So once a bubble is produced in a droplet containing dissolved NaCl, the salt accumulating at the interface during evaporation will diffuse to the bulk liquid much faster than in a Na$_2$SO$_4$ or MgSO$_4$ solution and thereby reduce the salt concentration. Consequently, the bubbles in NaCl solution will coalesce much more easily than in Na$_2$SO$_4$ and MgSO$_4$ solutions. At high concentrations, the reduction of vapor pressure and the increase in surface tension start to reduce the bubble growth rate greatly, resulting in an obvious increase in droplet lifetime.

3.4 Summary

Dissolving small amount of salts into water does not change the properties of the bulk water significantly; however, it may have significant effects on droplet boiling. Dissolved salts reduce the heat transfer in the evaporation region. Once the droplet is in a state of nucleation, dissolved salts may enhance the boiling heat transfer by inhibiting bubble coalescence. This effect is dependent on many properties of the solution, but the dominant property is the concentration of ions in the solution. If the coalescence of
growing bubbles is impeded and the pressure inside a bubble overcomes the liquid-solid surface tension, the growing bubbles will be able to expand the droplet and thereby enhance the boiling heat transfer significantly. This leads to the observed result that dissolved Na₂SO₄ and MgSO₄ can reduce the droplet lifetime with increasing salt concentration. Once the concentration of a dissolved salt in water reaches its transition concentration, the reduction will reach its maximum. If the concentration is increased further, it will produce an adverse effect, reducing droplet evaporation rate, since the dissolved salt lowers the vapor pressure.
4. EFFECT OF SALTS DECOMPOSING AT HIGH TEMPERATURE ON DROPLET BOILING

The study presented in Chapter 3 demonstrates that adding salts into water can improve droplet boiling heat transfer significantly. Those salts tested in Chapter 3 do not decompose within the surface temperature range used in this investigation; however, many other salts may decompose when heated. Since the dissociation process may produce gas in some cases, these salts may have the combined effects of both gases and salts on water droplet boiling when dissolved into water. To investigate the effects of these salts, sodium bicarbonate (NaHCO₃) was chosen as a typical compound because it decomposes at high temperature to form carbon dioxide (CO₂) and sodium carbonate (Na₂CO₃).

The decomposing process is:

\[2\text{NaHCO}_3(s) \leftrightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)\] (4.1)

The decomposition rate can be estimated by using kinetic data from the literature (Hu et al. 1986). Details of the calculation can be found in Appendix D. Since decomposition of dissolved sodium bicarbonate may produce the combined effects of the gas (carbon dioxide) and salt (sodium carbonate), both sodium carbonate and carbon dioxide were also examined separately to determine the single effect of each additive.

The study in this section classified droplet evaporation into three regimes based on the surface temperature. When pure water droplets were deposited on a stainless steel plate at a temperature below 120°C, the surface temperature was not high enough to trigger bubble nucleation and the droplets evaporated without nucleate boiling. When the surface temperature was increased above 120°C, droplets entered the nucleate boiling regime, and when the surface temperature was above 210°C droplets were in film boiling. In this study, the droplets containing additives were photographed on the hot surface at four
typical temperatures: 100°C (evaporation), 130°C (nucleate boiling), 210°C (transition film boiling), and 300°C (film boiling) to provide detailed information on the effects of these additives. Droplet lifetime within the temperature range from 100°C to 300°C was also recorded.

4.1 Droplet Behavior in the Evaporative Regime

Figure 4.1 shows photographs of water droplets, and those containing the three different additives considered in this section of the study, evaporating on a surface at 100°C. Each row in Fig. 4.1 shows a consecutive stage during the droplet lifetime.

A small air bubble was trapped at the center of a water droplet when it landed on the surface (see Fig. 4.1a, t=0.75 s). The bubble grew larger as the droplet evaporated. As the volume of liquid diminished, the liquid-solid contact angle decreased while the contact area between the droplet and substrate remained constant. Eventually, when the contact angle reached a lower limit, equal to the receding contact angle, the contact diameter began to decrease rapidly until the droplet disappeared. We measured the evolution of contact diameter and contact angle during droplet evaporation, with the results shown in Figure 4.2 and Figure 4.3 respectively. The contact diameter of pure water droplets was constant for t<20 s, after which it decreased rapidly.

We also calculated the surface area of the droplet exposed to air (from which liquid evaporated) by measuring the droplet height and diameter and assuming it to be a segment of a sphere (see Figure 4.4). In addition, the variation of water volume during evaporation was also calculated by subtracting the bubble volume from the droplet volume with the bubble simplified as a segment of an ellipse.
Figure 4.1  Evaporation of droplets on a surface at 100°C: a) pure water, b) water containing dissolved CO₂, c) 1% by weight solution of Na₂CO₃, d) 1% by weight solution of NaHCO₃
Figure 4.2 Variation of liquid-solid contact diameter with time during evaporation of droplets on a stainless steel surface at 100°C.
Figure 4.3  Variation of liquid-solid contact angle with time during evaporation of droplets on a stainless steel surface at 100°C.
Volume of a water droplet was given by:

\[ V_d = \frac{\pi}{3} R_d^2 (2R_d + \frac{C^3}{R_d^3} - 3C') \quad (4.2) \]

Where \( R_d \) (\( R_d = \frac{D'}{2} \)) is the radius of the sphere, \( C' \) and \( D' \) are calculated as follows:

\[ D' = H + \frac{D_d^2}{4H} \quad (4.3) \]
\[ C' = D' - H \quad (4.4) \]

Where \( D_d \) is the contact diameter and \( H \) is the height of the droplet.

Volume of the bubble inside was calculated by:

\[ V_b = \frac{\pi}{3} \left( \frac{D_b}{2} \right)^2 \left( 2h - \frac{c^3}{h^2} + 3c \right) \quad (4.5) \]
Where \( D_b \) is the diameter of the bubble, \( h \) is the height from the top to the center, and \( c \) is the distance from the center of the bubble to the surface.

The variations of droplet surface area and water volume are shown in Figure 4.5 and Figure 4.6 respectively, and a steady decrease in area corresponding to a similar change in water volume is evident as the droplet evaporates. The rate at which the surface area diminished increased towards the end of the droplet lifetime (\( t > 20 \) s) when the contact diameter began to shrink.

Addition of NaHCO\(_3\) to water droplets placed on a surface at 100°C led to an increase in their lifetime (Fig. 4.1 c and d), in agreement with the findings of King et al. (1997). Dissolving a salt in water is known to reduce its vapor pressure. The magnitude of this effect can be calculated using the method described by Cisternas et al. (1991). The calculation process and reference data are given in Appendix C. We estimated that the reduction of vapor pressure is small for dilute solutions: dissolving 1\% by weight of NaHCO\(_3\) and Na\(_2\)CO\(_3\) reduces the vapor pressure to 100 kPa at 100°C, only slightly lower than that of pure water (101 kPa). However, as the droplet evaporated and its salt concentration increased, the reduction in vapor pressure would become more pronounced. The decrease of vapor pressure would diminish the rate of mass transfer from the droplet surface and increase droplet evaporation time. The reduction of vapor pressure with increasing salt concentration is shown in Appendix B. King et al. (1997) developed a model to predict the evaporation rate of a small water droplet containing an additive by taking the droplet as a thin right circular cylinder with a thickness and an equivalent volume equal to the spherical segment and assuming a linear temperature profile within the droplet. They also showed that as the concentration of dissolved salt increased, the average evaporation rate became slower.

As the droplets of NaHCO\(_3\) solution evaporated salt crystals precipitated along their edges, where the evaporation rate was highest (see Fig. 4.1 d at \( t = 31.05 \) s). The ring
Figure 4.5  Variation of liquid-air interface area during evaporation of droplets on a stainless steel at 100°C.
Figure 4.6 Variation of water volume in the droplet on a hot surface at the temperature of 100°C with the evaporation time.
of salt prevented inward movement of liquid at the edge of the droplet as they grew smaller. In fact droplets spread out slightly towards the end of their life, as is evident in both photographs (see Fig. 4.1 d at \( t=26.55 \) s) and our measurements of droplet diameter (Fig. 4.2).

The salt stain left after all the water had evaporated was in the form of a circle along which there were regularly spaced fingers, perhaps created by a surface tension driven instability (Zhang et al., 1987). The assumed mechanism is shown Figure 4.7. During evaporation, vaporization of water left the salt molecules to accumulate at the interface between the droplet surface and air. These molecules formed a monolayer, creating a repulsive pressure that opposes the surface tension force. If the repulsive pressure exceeded the surface tension, the net effect was to cause the surface to expand, resulting in rippling of the surface. The effect propagated to the boundary of the drop and caused the boundary to migrate outward if it was large enough to overcome the coherence with the solid surface, as shown in Fig. 4.1d.

Dissolved \( \text{Na}_2\text{CO}_3 \) had a similar effect to \( \text{NaHCO}_3 \) on droplet evaporation except the gradual spreading of the droplet near the end of evaporation. The droplet diameter stayed constant during evaporation because the crystals precipitated around the edge of the droplet prevented the droplet from shrinking. It increased droplet evaporation lifetime slightly by reducing the vapor pressure of the water.

Dissolving \( \text{CO}_2 \) in a water droplet placed on a surface at 100°C slightly reduced its evaporation time (see Fig. 4.1b). Inspection of videotapes of evaporating droplets showed that several vapor bubbles nucleated within the drop immediately after it was deposited on the surface. These rapidly merged with each other, so that by \( t=0.75 \) s (the first frame in Fig. 4.1) there remained a single large bubble. The solubility of \( \text{CO}_2 \) decreases with rising temperature and gas escaping from the solution made the bubble much larger than that in a drop of pure water. The bubble produced little change in the
Figure 4.7 Thermal instability of a droplet induced by the ions accumulated at the liquid-air interface during evaporation of a droplet containing NaHCO₃.
contact diameter (Fig. 4.2), though it did increase the droplet surface area exposed to air (see Fig. 4.5, 0<t<5 s). The increased area for evaporation produced a small decrease in droplet lifetime. The effect is not very significant because, as shown by di Marzo and Evans (1989) and Chandra et al. (1996), most heat transfer to an evaporating droplet occurs around its edge where the substrate is hottest. Therefore the circumference, rather than surface area, principally determines droplet evaporation time.

4.2 Nucleate Boiling Behavior

Increasing the surface temperature to 130°C led to the formation of vapor bubbles in droplets deposited on the surface and the onset of nucleate boiling. Fig. 4.8 shows photographs of water droplets containing dissolved NaHCO₃ boiling on a surface at 130°C. To make a comparison with other additives, Figure 4.9 also shows photographs of pure water droplets (Fig. 4.9a), droplets containing dissolved CO₂ (Fig. 4.9b) and droplets with dissolved Na₂CO₃ (Fig. 4.9c) on a surface at 130°C. By examining the video record of droplet evaporation it was observed that a number of small bubbles formed in cavities on the heater surface nucleated inside the droplets immediately after impact. However, for pure water droplets these bubbles rapidly coalesced, so that by t=0.35 s (the first frame in Fig. 4.9) only one large bubble was evident. This bubble grew larger as the droplet evaporated, until it finally broke through the droplet surface. No more bubbles were produced in the droplet; as the liquid evaporated it cooled the stainless steel substrate further suppressing nucleation.

Dissolved NaHCO₃ had two significant effects on nucleate boiling of a water droplet (Figure 4.8). First, a large number of bubbles were visible in the droplet soon after impact (Fig. 4.8, t=0.35s), probably because of the CO₂ released by the decomposition of NaHCO₃. These bubbles did not coalesce but kept growing. Second, at
NaHCO₃ solution (1%)

- 40 ms
- 0.35 s
- 0.75 s
- 1.15 s
- 1.55 s
- 1.95 s

2.35 s
2.75 s
3.15 s
3.55 s

0 3 mm

Figure 4.8 Evaporation of 1% by weight solution of NaHCO₃ droplets on a hot surface at 130°C
Figure 4.9 Evolution of droplets on a hot surface at 130°C: a) pure water, b) water containing dissolved CO₂, c) 1% by weight solution of Na₂CO₃
approximately \( t = 1.2 \text{s} \), the abrupt nucleation of more bubbles was observed. The bubbles also did not coalesce but grew larger, greatly expanding the droplet diameter. The bubbles burst, reducing the droplet evaporation time by over half compared to that for pure water. The ability of dissolved salts to produce foaming was consistent with the findings in our previous experiments (Chapter 3).

The sudden nucleation of bubbles in the droplets of \( \text{NaHCO}_3 \) solution fragmented them and produced a large decrease in evaporation time (see Fig. 4.8 at \( t = 3.55 \text{s} \)). We believe that this was caused by salt particles precipitating from the evaporating droplet, which served as nuclei to trigger bubble formation. The particles were too small to observe directly, but to test our hypothesis we sprinkled a few salt particles on the hot surface before a droplet was deposited on it. These produced instantaneous nucleation of bubbles in water droplets landing on them.

Dissolved \( \text{NaHCO}_3 \) decomposed to form carbon dioxide and sodium carbonate during the droplet lifetime. The variations of decomposition rate and amount of carbon dioxide during evaporation were estimated using data from the literature (refer to Appendix D, Figure D.1 and Figure D.2). It was found that approximately 10% of the \( \text{NaHCO}_3 \) in a 1% by weight aqueous solution decomposed during the droplet lifetime. This would produce about 10% of the mass of \( \text{CO}_2 \) that could be dissolved in pure water, i.e. 0.07 mm\(^3\) of \( \text{CO}_2/\text{mm}^3 \) water (at STP). \( \text{CO}_2 \) was known to produce bubbles in the liquid and sodium carbonate has the ability to produce foaming by preventing bubble coalescence. So the effects of dissolved \( \text{NaHCO}_3 \) may be attributed to both of \( \text{CO}_2 \) and \( \text{Na}_2\text{CO}_3 \). To further explore the mechanism, the separate effects of the two products from the decomposition process were observed from photographs. A sample of these is shown in Fig. 4.9.

The boiling of a droplet of 1% by weight solution of \( \text{Na}_2\text{CO}_3 \) shown in Fig. 4.9 is similar to that for \( \text{NaHCO}_3 \) solution. Bubbles were produced immediately after the
droplet was deposited. These bubbles did not coalesce, but grew larger. A large number of new vapor bubbles were again observed at approximately $t=3$ s, much later than for the NaHCO$_3$ solution. The bubbles disrupted the droplet so that it evaporated in approximately 3.5 s.

Dissolving CO$_2$ in the droplet increased the number of bubbles present immediately after impact, and they coalesced to produce a large bubble so that by $t=0.35$ s (the first frame in Fig. 4.9b) only one large bubble was evident. The bubble grew larger as CO$_2$ came out of solution until it finally broke through the droplet surface. No more bubbles were produced in the droplet; as the liquid evaporated it cooled the stainless steel substrate too much to support further nucleation. Dissolved CO$_2$ increased the droplet diameter during the droplet boiling so that droplet evaporation time was, therefore, slightly reduced.

Our measurements of droplet evaporation time on surfaces at temperatures ($T_w$) ranging from 100°C to 210°C are shown in Fig. 4.10. Each data point represents the average of five measured values with error bars marking the highest and lowest measured values. To summarize our findings, at a low surface temperature ($T_w=100$°C), CO$_2$ reduced the evaporation time slightly, while the two salts increased it. At higher temperatures ($T_w>120$°C) both salts produced a large reduction in evaporation time, NaHCO$_3$ having a larger effect than Na$_2$CO$_3$.

### 4.3 Droplet Behavior on a Surface above 210°C

Droplets deposited on a surface at a temperature higher than 210°C went into a state of transition boiling. Water droplets evaporated so rapidly that the pressure of vapor generated at the liquid-solid interface was sufficient to lift them off the surface. Fig 4.11 shows three sequences of photographs of the impact and recoil of droplets of water (Fig.
Figure 4.10  Variation of droplet lifetime for droplets deposited on a stainless steel surface at temperatures ranging from 100°C to 210°C.
Figure 4.11 Impact of droplets on a surface at 220°C: a) pure water, b) water containing dissolved CO₂, and 1% by weight solution of NaHCO₃.
4.11a), water with dissolved CO₂ (Fig. 4.11b), and NaHCO₃ solution (Fig. 4.11c), on a surface at 220°C. Dissolved NaHCO₃ solution droplets had a visibly larger number of bubbles in them (see Fig. 4.11, t=1.1 ms) whose coalescence was inhibited by the salt. Bubbles bursting out of the liquid caused the droplet to disintegrate (t=5.3 ms). Since Na₂CO₃ had an effect similar to that of NaHCO₃, a separate set of photographs for Na₂CO₃ solution droplets is not shown. Dissolved CO₂ had no significant effect on droplet behavior, i.e. the droplets with dissolved CO₂ behaved much like the pure water droplets.

To record the evaporation time of droplets on surfaces with T_{s}>210°C, the droplets were deposited on a stainless steel plate machined to make the upper surface slightly concave, which prevented droplets from rolling off. Measured droplet lifetimes for 210°C≤T_{s}≤300°C are shown in Figure 4.12. Data for the two salt solutions is not shown, since the droplets splattered during impact, and it was not possible to define a meaningful evaporation time. There was little difference in measurement for pure water droplets and those with dissolved CO₂. Droplet evaporation times increased with substrate temperature for 210°C≤T_{s}≤240°C. The surface temperature corresponding to the maximum droplet evaporation time is known as the 'Leidenfrost temperature'. Above this droplets are fully levitated on a thin film of their own vapor, and are in a state of stable film boiling. Droplet evaporation times then decrease with further increases of temperature.

Figure 4.13 shows photographs of droplets landing on a surface at 300°C. Dissolved NaHCO₃ still promoted bubble nucleation, which was vigorous enough to breakup the droplet (Fig. 4.13c, t=7.5 ms). Droplets containing CO₂ had far fewer bubbles than those of pure water (see Fig. 4.13, t=1.5 ms). Vapor bubbles are formed by heterogeneous nucleation when liquid touches the solid surface. When a droplet approached the heated plate, dissolved CO₂ quickly escaped from the bulk liquid since
Figure 4.12 Variation of droplet lifetime for droplets deposited on a stainless steel surface at temperature ranging from 210°C to 300°C.
Figure 4.13  Impact of droplets on a surface at 300°C: a) pure water, b) water containing dissolved CO₂, and 1% NaHCO₃ solution (1%).
the solubility of CO₂ decreases sharply with increasing water temperature. Gas emerging from under the droplet would form a film that prevents liquid from contacting the hot substrate, suppressing nucleation. Jeschar et al (1996) have also noted that dissolved gas makes the vapor film formed around a heated sphere immersed in water more stable.

4.4 Summary

We observed the effects of dissolving either a gas (CO₂) or a salt (Na₂CO₃ or NaHCO₃), in water droplets impinging on a heated surface. At surface temperatures too low to initiate nucleate boiling it was found that droplet lifetime was determined by heat and mass transfer around the periphery of the droplet. In the evaporative regime, dissolved NaHCO₃ and Na₂CO₃ both reduced droplet evaporation rates since they lower the vapor pressure of water. Dissolved CO₂ enhanced the evaporation rate slightly, because the gas bubble trapped in the droplet made it swell and increased its circumference. In the nucleate boiling regime, Na₂CO₃ prevented coalescence of bubbles in the liquid and promoted foaming, reducing droplet evaporation times. Salt particles precipitated from the solution during evaporation also triggered vapor nucleation. Dissolved NaHCO₃ reduced droplet lifetimes even more than Na₂CO₃, because it decomposed when heated to produce CO₂, further augmenting bubble formation. When a droplet was deposited on a surface above the Leidenfrost temperature, dissolved CO₂ escaped from below the drop and prevented it touching the substrate, suppressing heterogeneous nucleation. Conversely, both salts promoted bubble nucleation and foaming so vigorously that droplets disintegrated upon impact.
5. EFFECT OF DISSOLVED SALTS ON SPRAY COOLING

5.1 Spray Parameters

Numerous studies concerning spray cooling have been carried out to determine the main parameters, prior to impingement upon the surface, governing the heat transfer coefficient in spray cooling. However, there are many disagreements among these studies concerning the effects of these spray parameters associated with spray cooling. Brimacombe et al. (1980) revealed that volumetric spray flux $Q''$ had the greatest influence on the heat transfer coefficient. Other parameters were also suggested to influence the spray heat transfer, namely droplet velocity, and droplet diameter (Bolle and Moureau, 1982, Yao and Choi, 1987). Recently, Mudawar and Valentine (1989) performed extensive experimental studies on spray quenching in film boiling, transition boiling, nucleate boiling, and single-phase cooling regimes. Table 5.1 is a summary of the correlations developed by Mudawar and Valentine (1989).

Table 5.1. Summary of Mudawar and Valentine’s spray cooling correlations (1989)

<table>
<thead>
<tr>
<th>Boiling(quenching) regime</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film boiling regime</td>
<td>$q'' = 63.250\Delta T^{1.091}Q^{0.284}d_{32}^{-0.062}$</td>
</tr>
</tbody>
</table>
| Transition boiling regime     | $\log_{10}\left(\frac{q''}{q''_{max}}\right) = 4.78 \times 10^{5}\left(\frac{U_m}{Q''}\right)^{-1.255}\left(\log_{10}\left(\frac{T_s - T_f}{T_{max} - T_f}\right)\right)^3$
  $-1.90 \times 10^4\left(\frac{U_m}{Q''}\right)^{-0.903}\left(\log_{10}\left(\frac{T_s - T_f}{T_{max} - T_f}\right)\right)^2$ |
| Critical heat flux            | $\frac{q''}{\rho_s h_f Q''} = 122.4 \left[1 + 0.0118\left(\frac{\rho_f}{\rho_s}\right)^{1/4}\left(\frac{\rho_f c_p f \Delta T_{sub}}{\rho_s h_f}\right)\left(\frac{\sigma}{\rho_f Q''^{0.5} d_{32}}\right)^{0.198}\right]$ |
$$T_{\text{max}} = 18 \left[ (\rho_s h_f Q''') \left( \frac{\sigma}{\rho_f Q''^2 d_{32}} \right)^{0.198} \right]^{1/5.55} + T_f$$

Nucleate boiling regime

$$q'' = 1.87 \times 10^{-5} (T_x - T_f)^{5.55}$$

Onset of single-phase regime

$$T_x = 13.43 \text{Re}^{0.167} \text{Pr}_f^{0.123} \left( \frac{k_e}{d_{32}} \right)^{0.220} + T_f$$

Single-phase regime

$$Nu = 2.512 \text{Re}^{0.76} \text{Pr}_f^{0.56}$$

where $q''$ is in W/m², and $T_x$ and $T_f$ are in °C.

They singled out three parameters as influencing, to various degree depending on boiling regime, the heat flux: volumetric spray flux $Q''$, Sauter mean diameter, $d_{32}$, and mean droplet velocity, $U_m$.

Sauter mean diameter (SMD, $d_{32}$) is a means of expressing the fineness of a spray in terms of the surface area produced by the spray. Sauter mean diameter is defined as the diameter of a drop having the same volume-to-surface area ratio as the total volume of all the drops to the total surface area of all the drops. Sauter mean diameter obtained by the nozzles in this study was predicted using the following correlation developed by Esters et al. (1995) for water sprayed from full cone nozzles.

$$\frac{d_{32}}{d_0} = 3.67 (\text{We}_{d_0}^{1/2} \text{Re}_{d_0})^{-0.259} \quad (5.1)$$

The characteristic length and velocity chosen for correlating the SMD in this correlation were the orifice diameter, $d_0$, and liquid velocity at the orifice, defined as $(2\Delta P/\rho_f)^{0.5}$. The Weber and Reynold numbers based on the orifice conditions were defined, respectively, as

$$\text{We}_{d_0} = \frac{\rho_a (2\Delta P / \rho_f) d_0}{\sigma} \quad (5.2)$$

and
\[
\text{Re}_{d_0} = \frac{\rho_f (2\Delta P/\rho_f)^{1/2} d_0}{\mu_f}
\]

(5.3)

where \(\rho_a\) is the density of ambient fluid (air or vapor).

Using a simple energy balance analysis, the mean velocity \((U_m)\) of droplets impinging upon the test surface was estimated from the following correlation developed by Ghodhane et al. (1991) and extended by Qiao (1996).

\[
U_m = (U_0^2 + \frac{2\Delta p}{\rho} - \frac{12\sigma}{\rho d_{os}} - 2g\Delta h \sin(\alpha))^{1/2}
\]

(5.4)

where \(U_0\) denotes the upstream velocity; \(\Delta p\) the pressure difference between upstream and downstream (ambient pressure); \(\rho\) the density of the liquid; \(g\) the acceleration of gravity; \(\Delta h\) distance between the nozzle and test surface and \(\alpha\) angle of surface inclinations which varies from \(-90^\circ\) for a downward facing surface, \(0^\circ\) for a vertical surface to \(90^\circ\) for an upward facing surface. The test surface in this study faced downward for temperature measurement and upward for photography. \(d_{os}\) represents mass median diameter most commonly applied in spray heat transfer as a means of expressing drop size in terms of the volume of liquid sprayed. The mass median diameter when measured in terms of volume is a value where 50% of the total volume of the liquid sprayed is made up of drops with diameters larger than the median value \((d_{os})\) and 50% of the drops have diameters smaller than the median value \((d_{os})\). Mass median diameters used in this study were provided by the nozzle manufacturer. The equation can be simplified by keeping the second term on the right hand side of Eq. (5.4) and neglecting the other three terms without producing an error of greater than 1%.

Two commercial full cone nozzles (Unijet TG 0.6 and TG 0.7, Spray Systems Co., Wheaton, IL) were employed in this study to achieve two different mass fluxes sprayed on the surface: 0.5 and 3.0 kg/m\(^2\)s, respectively. They provided uniform coverage over the test surface. Table 5.2 summarizes the range of experimental variables obtained...
by different combinations of spray nozzles, operating pressures and varying the nozzle-to-surface distance.

Table 5.2 Summary of spray variables

<table>
<thead>
<tr>
<th>case #</th>
<th>nozzle #</th>
<th>spray pressure (kPa)</th>
<th>distance (mm)</th>
<th>mass flux (kg/m²s)</th>
<th>d₀₅ (mm)</th>
<th>Uₘ (m/s)</th>
<th>d₃₂ (mm)</th>
</tr>
</thead>
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<td>0.60</td>
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<td>0.191</td>
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<td>0.54</td>
<td>20</td>
<td>0.172</td>
</tr>
<tr>
<td>3</td>
<td>TG0.6</td>
<td>276</td>
<td>100</td>
<td>0.5</td>
<td>0.50</td>
<td>23</td>
<td>0.160</td>
</tr>
<tr>
<td>4</td>
<td>TG0.7</td>
<td>138</td>
<td>52.5</td>
<td>3.0</td>
<td>0.70</td>
<td>17</td>
<td>0.204</td>
</tr>
<tr>
<td>5</td>
<td>TG0.7</td>
<td>207</td>
<td>50</td>
<td>3.0</td>
<td>0.64</td>
<td>20</td>
<td>0.184</td>
</tr>
<tr>
<td>6</td>
<td>TG0.7</td>
<td>276</td>
<td>48.6</td>
<td>3.0</td>
<td>0.58</td>
<td>23</td>
<td>0.170</td>
</tr>
</tbody>
</table>

Adding small amount of a salt into water was found to increase surface tension and viscosity by less than 1% (refer to Appendix C). Therefore, no significant change in Sauter mean diameter was expected. Mudawar and Valentine (1989) found that the heat transfer coefficient was very sensitive to variations in volumetric flux over all regimes; mean drop velocity was also important in transition boiling and Sauter mean diameter in the single-phase regimes. In the nucleate boiling regime, the heat transfer was a function of surface temperature alone, unaffected by variations in spray hydrodynamics. Hoogendorn and den Hond (1974) also obtained similar results, finding that varying Sauter mean diameters in the range 0.2 to 1 mm had little impact on spray cooling. Yao and Choi (1987), studying spray cooling using a mono-size spray, came to the same conclusion. Therefore, any spray cooling enhancement in the nucleate boiling and transition boiling regimes can be attributed to the addition of the salts rather than any change in droplet size and distribution, taking into consideration that Sauter mean
diameter plays a very weak role in spray cooling in the nucleate and transition boiling regimes.

5.2 Spray Cooling of a Hot Surface

Figure 5.1 displays typical temperature measurements made during spray cooling of a surface using pure water with a mass flux $m_i=0.5$ kg/m$^2$s. The temperature variation recorded by each of the four thermocouples ($T_1$ to $T_4$) is shown. Prior to spray cooling, the test surface was heated and its temperature held constant at 240°C. Heat conduction in copper was high enough to give an almost uniform temperature profile along the centerline. The temperature difference between the top thermocouple and the bottom one was less than 1°C at the instant that water was sprayed on the test surface, and increased with spray cooling up to approximately 10°C. The response of the point away from the quenched surface was considerably delayed relative to the point closer to the surface. The temperature measured by the thermocouple closest to the surface dropped from 240°C to 100°C in approximately 250 s, during which the bottom one dropped from 240°C to 110°C.

Figure 5.2 demonstrates the variation of heat flux and surface temperature with spray cooling. The heat flux was calculated using the sequential method to solve the inverse heat conduction problem (IHCP, Beck et al., 1985), and the surface temperature was extrapolated from the interior temperature measurements in Figure 5.1 assuming one-dimensional heat conduction within the test block. The accuracy of the temperature measurements was estimated to be ±0.5°C, and the embedded thermocouples were positioned within ±0.15mm. The errors in the temperature measurements and positions of the thermocouples could produce an error in the calculation of heat flux of, at most, up to 10 percent, with the largest errors occurring at the start and the end of cooling where
Figure 5.1 Transient temperature measurements during spray cooling using pure water.
Figure 5.2  Calculated surface heat flux and temperature during spray cooling obtained from interior temperature measurements of Figure 5.1.

\[ m_i = 0.5 \text{ kg/m}^2\text{s} \]
\[ U_m = 20 \text{ m/s} \]
\[ d_{os} = 0.54 \text{ mm} \]
the relative magnitude of heat flux was small (Qiao, 1996). In this spray cooling process, the hot surface experienced four different heat transfer regimes: film boiling, transition boiling, nucleate boiling, and single-phase liquid cooling. The cooling commenced in the film boiling regime, in which a thermally insulating vapor layer developed on the surface, resulting in a relatively slow cooling process \( q'' = 0.03 \text{ MW/m}^2 \). Better liquid-surface contact was maintained once the surface temperature dropped below the minimum heat flux point, leading to the transition boiling regime (220°C to 140°C). Heat transfer increased significantly in the transition boiling regime until the surface temperature dropped below the critical heat flux point \( q'' = 0.26 \text{ MW/m}^2 \). Heat transfer decreased quickly with further reduction in surface temperature in the nucleate boiling regime (140°C to 105°C). Once the surface temperature became too low to sustain bubble nucleation, cooling was in the slow, single-phase liquid cooling regime \( q'' \leq 0.08 \text{ MW/m}^2 \).

5.3 Effect of Dissolved Salts on Spray Cooling

The effect of dissolved salts on spray cooling was tested using the solutions of NaCl, Na\(_2\)SO\(_4\), and MgSO\(_4\) with concentration of 0.6 mol/L. Photographs, representatives of the spray cooling process with different dissolved salts under the same operating conditions as those used to produce Fig. 5.1 and Fig. 5.2, were taken. They are shown in Figure 5.3 and Figure 5.4. When the hot surface was quenched with pure water, initially at 240°C, heat transfer was in a state of film boiling, in which no droplets were seen on the surface. Since the droplets sprayed on the surface were small \( d_{32} = 0.2\text{mm} \) relative to the quenched surface \( d = 25.4\text{mm} \), they were not visible on the photographs prior to impinging on the surface. Droplets from the nozzle impacted and spread on the hot surface, and then were lifted off the surface by a thin layer of vapor film. The
Figure 5.3  Photographs of droplet impact during spray cooling of pure water
Figure 5.4: Photographs of droplet impact during spray cooling of NaCl, Na₂SO₄, and MgSO₄ solutions.
Figure 5.4 Continued
residence time of droplets on the surface was very short. The surface was quenched with a light spray of water (0.5 kg/m²s) rather than a dense spray, so the interaction among the droplets sprayed on the surface was very weak. Therefore, droplets were prevented by the short droplet residence on the surface and weak droplet interaction from coalescing to form big visible droplets on the surface. The spray cooled the surface relatively slowly down to the 220°C in 60 s, leading to transition boiling (220°C to 140°C). In the transition boiling regime, a few separate big droplets, which were estimated to be three times the spray droplets in size, were first seen on the surface at 160°C (see Fig. 5.3). We believe that this was caused by droplet coalescence. Droplets impacted and broke up into many smaller single droplets, which coalesced to form big visible droplets. Once the surface temperature decreased below the critical heat flux point (140°C), heat transfer entered the nucleate boiling regime. Since the liquid/solid contact angle for pure water is large (~90°), droplets after impact did not spread but recoiled, finally coming to rest as hemispherical masses on the surface (see Fig. 5.3 at 135°C) instead of forming a continuous film on the surface. Droplets agglomerated to form visible masses on the surface, decreasing the contact area between the droplets and surface. Heat flux was aggressively reduced by the wall temperature drop and reduction of the contact area. Finally, as the surface temperature continued to drop below 110°C, which was the minimum temperature to initiate nucleation, the nucleation was suppressed. Heat transfer was in a state of single-phase liquid cooling, in which the surface could not evaporate the water quickly enough, leaving the water to reside on the surface. The surface was completely covered with a layer of water at 105°C (see Fig. 5.3).

Dissolving salts in water produced several visible changes in the quenching process. Photographs taken of a surface cooled with dissolved salt solutions are displayed in Fig. 5.4, in which different effects on spray cooling caused by different salts are also exhibited. When the surface was quenched with the NaCl solution (row a) initially at
240°C, NaCl particles were first seen on the surface at 160°C, and then accumulated to form a uniform layer of salt particles. In the film and transition boiling regimes (T_a=240°C to 140°C), the droplets sprayed on the surface evaporated quickly, leaving fine salt particles on the surface, which reduced the reflectivity of the test surface. The thickness of the particle layer increased until the surface temperature dropped below 140°C, at which point droplets started to rewet the surface and flush the salt particles off the test cylinder. The accumulation of water, which occurred on the surface cooled with pure water, was not observed at the same surface temperature (T_a=135°C). We believed that, as dissolved salts in the droplets enhanced heat transfer, droplets evaporated quickly so that there were not enough droplets to agglomerate.

With the surface temperature decreasing, separate patches of liquid film were observed to occur on the surface and coalesce to form a thin liquid film, covering the surface. Once the surface was covered with liquid, it became brighter because the liquid film was more reflective than the salt particle film. In the nucleate boiling regime, dissolved salts inhibited bubble nucleation, producing more vigorous foaming, which was seen in the temperature range from 140°C to 110°C (see Fig 5.4). Bubble nucleation was suppressed completely when the surface was cooled below the same temperature as in the case of pure water (110°C). The cooling processes with Na_2SO_4 and MgSO_4 were similar to that of NaCl, but foaming was more vigorous in the film covering the face, especially in the case of MgSO_4. When the surface was quenched with MgSO_4 solution, several spots first appeared on the surface at 180°C. These spots were caused by agglomeration of precipitated particles of MgSO_4, which has a much lower solubility than the other two salts (see Figure B.3 in Appendix B). These spots increased the surface roughness, enhancing spray cooling. Once heat transfer entered the nucleate boiling regime, MgSO_4 had more discernable effect on reducing bubble coalescence and produced more vigorous foaming than NaCl.
Figure 5.5 shows the effect of dissolved salts on spray cooling heat transfer at a mass flux of 0.5 kg/m$^2$s. The most significant effect the dissolved salts had on boiling heat transfer was to increase both transition boiling and nucleate boiling heat flux in spray cooling. The effect of the dissolved salts on heat transfer in spray cooling was different from that in pool boiling, where dissolved salts were found to decrease the heat transfer coefficient. The critical heat flux point (140°C) was not changed greatly, but the heat transfer rate was increased by up to 20%. This is different from the effect of surfactants, which enhance nucleate boiling and single phase liquid cooling. As for the effect of dissolved salts in the film boiling regime ($T_w=240^\circ$ to 220°C), the boiling curves are very close except for the MgSO$_4$ curve. Dissolved salts had different effects on the heat transfer rate during spray cooling process; MgSO$_4$ had the biggest effect, Na$_2$SO$_4$ the second, and NaCl the lowest. These results agree with the earlier experimental study on the evaporation of single droplets of water containing dissolved salts. In the transition regime (220°C to 140°C), dissolved salts were found to inhibit bubble coalescence and break up the droplets into small droplets, resulting in more contact area between the droplet and the hot surface. In the nucleate boiling regime (140°C to 110°C), dissolved salts inhibited bubble coalescence and produced foaming, though the dissolved salts increased the surface tension of water and reduced the nucleation rate slightly. Dissolved MgSO$_4$ had a more significant effect on the heat transfer rate in the transition regime (see Fig. 5.5), where dissolved MgSO$_4$ particles stuck to the surface at high surface temperature (see Fig. 5.4) and increased the surface roughness, enhancing heat transfer.

The effect of dissolved salts on spray cooling heat transfer at high mass flux is shown in Figure 5.6, where the measured variation of surface heat flux with surface temperature was plotted for the pure water and the salt solutions at a mass flux of 3.0 kg/m$^2$s. The effect of dissolved salts on heat transfer rate was significantly increased with the increase in mass flux in the transition and nucleate boiling regimes, although the heat
Figure 5.5 The effect of the dissolved salts on heat transfer in the spray cooling at the mass flux of 0.5 kg/m²s
Figure 5.6  The effect of dissolved salts on spray cooling of a surface with water containing dissolved salts at a mass flux of 3.0 kg/m²s.
transfer rate still did not have a visible effect in the film boiling and the liquid evaporation regimes. Dissolved NaCl, Na₂SO₄, and MgSO₄ increased the critical heat flux by up to 40%, 70%, and 80%, respectively. The critical heat flux point, at which the droplets started to be levitated by the vapor, was not influenced by the changes in dissolved salts and mass flux of water sprayed on the test surface. As mentioned earlier, dissolved salts played an important role in bubble nucleation, which determined the heat transfer rate in the liquid remaining on the surface. Ions dissociated from the salts accumulated on the interface of the bubbles and retarded bubble coalescence, producing foaming which significantly increased heat transfer in the liquid.

The effect of the dissolved salts on the critical heat flux is shown in Figure 5.7, where the variation of the critical heat flux with the ionic strength of the dissolved salts in the solution is plotted for the selected salts under the same operation conditions as those used to produce the data shown in Fig.5.6. The critical heat flux for pure water was approximately 1.74 MW/m², while the critical heat flux for NaCl solution (0.06M) was 2.2 MW/m², Na₂SO₄ solution 2.5 MW/m², and MgSO₄ solution 2.75 MW/m². When spray cooling a surface, the critical heat flux during the cooling process was approximately proportional to the ionic strength (I) of the dissolved salt in the solution. This is consistent with the results of the single droplet experiments. It is confirmed that dissolved salts produced foaming and determined the heat transfer rate during a spray cooling process in the transition and nucleate boiling regimes.

5.4 Effect of Droplet Velocity on Spray Cooling

The effect of dissolved salts on the heat transfer rate during spray cooling is shown in Figure 5.8 for pure water and MgSO₄ (0.06M) at three different droplet velocities: 17 m/s, 20 m/s, and 23 m/s. As mentioned before, droplet velocity is an
Figure 5.7  The effect of dissolved salts on the critical heat flux at a mass flux of 3.0 kg/m²s.
Figure 5.8  The effect of dissolved salts on heat transfer rate during the spray cooling for pure water and MgSO$_4$ (0.06M) at three different droplet velocities: 17 m/s, 20 m/s, and 23 m/s.
important factor governing the heat transfer rate (see Table 5.1). Heat transfer rate during spray cooling was increased with increasing droplet velocity; the critical heat flux for pure water was increased from 1.7 MW/m² to 2.15 MW/m² when the droplet velocity increased from 17 m/s to 23 m/s. Increasing droplet velocity even improved the heat transfer rate in the film and single-phase regimes, in which the boiling curve slope was higher. At higher velocity, the droplets with higher kinetic energy impacted and spread to a larger diameter, resulting in more contact area between the droplet and the surface.

The Leidenfrost temperature (LFP), corresponding to the minimum heat flux, increased (see Fig. 5.8). Due to the limit of the surface temperature used in the experiments, we had difficulty in clearly determining the change in the Leidenfrost temperature. We believed that the increase in Leidenfrost temperature (LFP) was caused by the suppression of bubble nucleation at higher droplet velocities. Dissolving salt in the water significantly improved the heat transfer rate at all the three droplet velocities tested, making the changes in Leipenfrost temperature more obvious (see Fig. 5.8). Increasing impact velocity enhanced heat transfer for surface temperatures above 110°C when the surface was not flooded. At lower temperature, droplets impacted on the liquid film covering the surface and had little effect on heat transfer between the liquid and the surface. Our experiments confirmed the findings of Mudawar and Valentine (1989) and Klinzing et al. (1992) who reported that nucleate boiling heat transfer during spray cooling depends only on the surface temperature. The correlation proposed by Mudawar and Valentine (1989) accurately predicted our measured values of heat flux for pure water (see Fig. 5.8). However, our measurement of critical heat flux was different from the calculated value, although the spray parameters in our experiments were similar to theirs. This difference may be due to surface roughness, wettability, and time interval. Surface roughness and wettability are known to greatly influence the critical flux during spray cooling (Pais et al., 1992). The heat flux from the surface was very sensitive to the
time interval, which may produce uncertainty in measurement of the calculated heat flux by up to 40%. The heat flux calculated in our experiments increased with as the time interval was shortened until it reached a limit. However, the smaller the time interval, the more rough the boiling curve. For one test the time interval of 0.025 s was employed in the calculation of heat flux, the boiling curve was too rough to read. The heat flux measured in our experiments was calculated using the time internal of 0.125s. Dissolving salts enhanced boiling heat transfer at all velocities in the nucleate and transition boiling regions.

5.5 Effect of Salt Concentration on Spray Cooling

The effect of salt concentration on heat flux during spray cooling is shown in Figure 5.9. Pure water and MgSO₄ solutions at a mass flux of 3.0 kg/m²s and droplet velocity of 20 m/s are shown. We employed four concentrations in our experiments: 0.01M, 0.06M, 0.2M, and 0.4M. Heat transfer in spray cooling was only slightly enhanced by the dissolved salt at low concentration (0.01M), while heat transfer rate was greatly increased by the salt at the concentration of 0.06M. Dissolving more than 0.2M of salt reduced the heat transfer rate during spray cooling, since the dissolved salt reduced the vapor pressure of the liquid. Aside from the enhancement of heat flux in the transition and nucleate boiling regimes, dissolved MgSO₄ also greatly increased the heat transfer rate in the film boiling regime (see Fig. 5.9). The slope of the boiling curve for spray cooling with a MgSO₄ (0.04M) solution at temperatures near 240°C was higher than that for spray cooling with pure water. This implies that the dissolved salt significantly increased the Leidenfrost temperature. It was increased by at least 20°C and thereby heat transfer at temperature near 240°C was still in transition boiling. We believe that this was
Figure 5.9  The effect of salt concentration on heat flux during spray cooling for pure water and MgSO$_4$ solution at the mass flux of 3.0 kg/m$^2$s and droplet velocity of 20 m/s.
caused by salt precipitating on the surface and increasing surface roughness. Firstly, the dissolved salt vigorously broke up the droplets impacting on the surface by inhibiting bubble coalescence, retarding formation of the vapor layer and thereby increasing the Leidenfrost temperature. This observation agrees with the conclusion obtained in single droplet boiling. Secondly, the salt particles left from the previous drops increased the surface roughness. Surface roughness was reported to greatly increase the LFP for the droplet boiling on particle blasted and rough sanded surfaces by up to 90°C (Bernardin et al. 1999). The surface roughness dependence of the Leidenfrost temperature was speculated to be related to intermittent liquid-solid contact caused by surface aspirates poking through the thin vapor layer which, as reported by Labeish (1994), is on the order of 1μm. As the surface roughness increased, a thicker vapor layer, and hence a higher surface temperature, was required to keep the liquid fully separated from the solid surface. Finally, the surface deposits left from the previous drops tended to serve as bubble nucleation sites when making contact with newly impacted drops. This finding was consistent with those of Baumeister et al. (1970) and Bernardin et al. (1999), who reported that the Leidenfrost temperature for water on a wiped aluminum surface was 171°C, 54°C less than of an unwiped contaminated surface. Our experiments also confirmed the findings of Bolle and Moreau (1982), who reported that heat flux in film boiling regime was a weak function of both surface temperature and liquid subcooling. In addition, heat flux was found to increase only slightly with increasing droplet velocity and was nearly independent of droplet diameter.

The effect of dissolved salt concentration on critical heat flux during spray cooling is shown in Figure 5.10. It is obvious that a transition concentration existed in the inhibition of bubble coalescence (see Fig. 5.10). Once the concentration reached a limit (transition concentration), the dissolved salt inhibited most of the bubble coalescence processes in
Figure 5.10  The effect of dissolved salt concentration on critical heat flux during spray cooling.

\[ m_l = 3.0 \text{ kg/m}^2\text{s} \]

\[ U_m = 20 \text{ m/s} \]
the boiling liquid, producing foaming. This is consistent with the findings in the single droplet experiments.

The effect of dissolved salts on the surface temperature drop during spray cooling is shown in Figure 5.11 for \( m_i = 3.0 \text{ kg/m}^2\text{s} \) and \( U_m = 20 \text{ m/s} \). The dissolved salt \( \text{MgSO}_4 \) greatly changed the surface temperature response. When quenched with pure water from an initial temperature of 240°C, the cooling rate was relatively slow because spray droplets were initially in transition boiling and redound off the surface after impact. Dissolving small amounts of \( \text{MgSO}_4 \) (0.01M) did not have a visible effect on the surface temperature drop during spray cooling (see Fig. 5.11). However, dissolving \( \text{MgSO}_4 \) to a high concentration significantly increased the temperature drop rate. No relatively slow cooling was observed in Fig. 5.11. The time for cooling of a surface from 240°C to 100°C was reduced by the dissolved salt from 10 s to 2 s. This reduction in cooling time may be very beneficial to fire fighting and metal quenching processes, where the water consumption is critical. The temperature, below which bubble nucleation was completely suppressed by the cold surface, was not changed significantly. In fact, the presence of dissolved salt increased vapor pressure and thereby reduced the heat transfer from the surface. This was confirmed in the experiments of single droplet boiling.

5.6 Summary

The major findings in this chapter can be summarized as follows:

1) Dissolving salts in water significantly enhanced the heat transfer rate in the transition and nucleate boiling regimes during spray cooling. The increase in heat transfer rate was observed at all mass fluxes, impact velocities and concentrations in our experiments. The enhancement in heat transfer was mainly attributed to the inhibition of bubble coalescence and foaming caused by the dissolved salts.
Figure 5.11  The effect of dissolved salts on the surface temperature drop during spray cooling.

- pure water
- MgSO$_4$(0.01M)
- MgSO$_4$(0.06M)
- MgSO$_4$(0.4M)

$m_l = 3.0 \text{ kg/m}^2\text{s}$
$U_m = 20 \text{ m/s}$
2) The enhancement of critical heat flux induced by the dissolved salts increased with the molar concentration of the dissolved salts in water until the concentration reached the transition concentration. The measured transition concentration for spray cooling agreed with that for single droplet boiling very well.

3) The salt particles remaining on the surface also played a role in enhancement of spray cooling, because they increased the roughness of the test surface.

4) Dissolving the salts into water over the transition concentration produced adverse effect on spray cooling due to the reduction of the vapor pressure.

5) The dissolved salts increased the Leidenfrost temperature and thereby improved the heat transfer in the film boiling region. The time for cooling of a surface from 240°C to 100°C was reduced to 25% of that for a pure water spray.

6) Dissolved salts had little effect on the heat transfer from the surface in the evaporation region. Dissolved salts may reduce the spray cooling due to reduction of vapor pressure.
6. CONCLUSIONS

Experiments were done to: 1) investigate the effect of dissolved salts on boiling of a droplet on a hot surface, 2) examine the effect of dissolved salts decomposing at high temperature on droplet boiling, and 3) determine the effect of dissolved salts on spray cooling.

Several salts were chosen to examine the effect of dissolved salts on droplet boiling. Dissolving small amounts of salts into water does not change the properties of the water significantly; however, they may greatly affect droplet boiling. Dissolved salts reduce heat transfer during evaporation. Once the droplet is in a state of nucleate boiling, dissolved salts may enhance the boiling heat transfer by inhibiting bubble coalescence. This effect is dependent on many properties of the solution such as ions, viscosity, and vapor partial pressure, but the dominant property is the ions in the solution. If the growing bubbles in a droplet are prevented from coalescing, the pressure inside the bubbles may overcome the surface tension and the growing bubbles will be able to expand the droplet and thereby enhance the boiling heat transfer significantly. Dissolved Na₂SO₄ and MgSO₄ can reduce the droplet lifetime. Once the concentration of dissolved salt in water reaches its transition concentration, the maximum reduction in droplet lifetime will be achieved. If the concentration continues to increase, the droplet lifetime will increase since the dissolved salts reduce the vapor pressure. Dissolved NaCl has no obvious effect on droplet boiling at low concentration, while it increases the droplet boiling at high concentration. Dissolved salts always increase the departure from the nucleate boiling point by retarding bubble coalescence.

The effect of sodium bicarbonate (NaHCO₃), which decomposes to form carbon dioxide (CO₂) and sodium carbonate (Na₂CO₃) at high temperature, on droplet boiling was also investigated. Since decomposition of dissolved sodium bicarbonate may
produce the combined effects of the gas (carbon dioxide) and salt (sodium carbonate), both sodium carbonate and carbon dioxide were also examined separately to determine the single effect of each additive. At surface temperatures too low to initiate nucleate boiling it was found that droplet lifetime was determined by heat and mass transfer around the circumference of the droplet. Dissolved NaHCO₃ and Na₂CO₃ both reduced droplet evaporation rates since they lowered the vapor pressure of the liquid. Dissolved CO₂ enhanced the evaporation rate slightly, because the gas bubble trapped in the droplet made it swell and increased its circumference. In the nucleate boiling regime, Na₂CO₃ prevented coalescence of bubbles in the liquid and promoted foaming, reducing droplet evaporation times. Salt particles precipitated from the solution during evaporation also triggered vapor nucleation. Dissolved NaHCO₃ reduced droplet lifetimes even more than Na₂CO₃, because it decomposed when heated to produce CO₂, further augmenting bubble formation. When a droplet was deposited on a surface above the Leidenfrost temperature, dissolved CO₂ escaped from below the drop and prevented it touching the substrate, suppressing heterogeneous nucleation. Conversely, both salts promoted bubble nucleation and foaming so vigorously that droplets disintegrated upon impact.

Experiments on spray cooling were conducted in this study to investigate the effect of dissolved salts (NaCl, Na₂SO₄, MgSO₄, NaHCO₃). The results were compared with those obtained using pure water sprays. Dissolving salts in water significantly enhanced the heat transfer rate in the transition and nucleate boiling regimes during spray cooling. The increase in heat transfer rate was observed at all mass fluxes and impact velocities as well as concentrations in our experiments. The enhancement of critical heat flux caused by the dissolved salts increased with the molar concentration of the dissolved salts in water until the concentration reached the transition concentration. The enhancement in heat transfer was mainly attributed to the inhibition of bubble coalescence and foaming caused by the dissolved salts. The salt particles remaining on
the surface also played a role in enhancement of spray cooling, because they increased
the transient roughness of the test surface. Even though the particles covering the surface
produced thermal resistance between the droplets and the surface, the general effect was
to increase the heat transfer rate. The enhancement of the heat transfer rate by dissolving
the same molar concentration of salts in water was in the order of the ionic strength in the
solution. That is in the order of MgSO₄, Na₂SO₄, and NaCl from most to least
enhancement. Dissolving the salts in water a concentration above the transition
concentration reduced spray cooling heat transfer due to the reduction of the vapor
pressure. The measured transition concentration for spray cooling agreed with that for
single droplet boiling very well. The dissolved salts increased the Leidenfrost
temperature and thereby improved heat transfer in the film boiling region. The time for
cooling of a surface from 240°C to 100°C was reduced by up to 400%. Once the surface
temperature dropped below 105°C, below which nucleation was completely suppressed,
dissolved salts had little effect on heat transfer from the surface. In the regime, the
dissolved salts may decrease spray cooling due to the reduction of vapor pressure.
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Natelson Microgasometer Models # 600 and 650# Manual, Scientific Industries, Inc.


APPENDICES

Appendix A  Data Acquisition and Control (DAC) System

A.1 Single Droplet DAC System

To capture history of droplet impact on a hot surface, an electronic timing circuit with a droplet detector and a time delay circuit described by Qiao (1996) in greater detail was used. The timing circuit specifically designed and built for this study detected detachment of a droplet and triggered the flash unit and camera with a resolution of 1μs. Photographs of droplet evaporation were taken using this timing circuit and Labview VIs. Detachment of a droplet was detected by the timing circuit, and the shot time was varied by a data acquisition and control system (DAC). Once the droplet detached from the tip of the hypodermic needle, it generated a peak to peak pulse through the time delay circuit (the delay time was set 0 ms) to the data acquisition system. Setting the flash at the speed of 1/1000s allowed the camera to take high quality photographs of droplet evaporation.

Figure A.1 shows the VI of the control system. This VI works with the PCI-MIO-16E-4 board and SCB-68. Two built-in counters are used to count the time after droplet impact and vary delay time to send a pulse signal to a bounce free circuit, triggering the camera. The Event or Time Counter Config VI configures counter 1 to count the number of rising edges of a TTL signal at its Source INPUT pin. The Counter Start VI begins the counting operation for counter. The Counter Read VI returns until the STOP button is pressed or an error occurs. Finally, the Counter Stop VI stops the counter operation. Once the Event VI received a signal and sent a value to the Generated Delayed Pulse VI, the Generated Delayed Pulse VI varied the delay time and generated pulse trains. In this VI,
the edges of the internal SOURCE signal are counted to generate the output signal, the GATE is not used (software start) and the pulse signal on the OUT pin gets connected to the SCB-68 device. The delay time is varied by changing the pulse width. The signal from the electronic time delay circuit is connected to Channel 1 and the trigger pulse signal is sent to a bounce free circuit.

A.2 Spray Cooling DAC System

A.2.1 Camera Control System

Figure A.2 shows the DAC system, which receives the temperature signal from the 5B37 input and sends the pulse to the camera, depending on the input temperature. The AI Read One Scan VI configures the DAQ device (PCI-MIO-16E-4 board) to acquire data from analog channel 0, it performs calculation and evaluation on the data and determines whether the Generate Pulse VI (described above) outputs the pulse signal to the camera. Because the iteration count is connected to AI Read One Scan, the application configures the DAQ device for analogy input only on the first iteration of the loop. The loop rate as well as the acquisition rate is specified by the loop rate (50 ms). Since a large number of large-sized front panel indicators, like charts and graphs, affect the control rate, only a few front panel indicators are kept to precisely control the loop.

A.2.2 Temperature Acquisition System

Figure A.3 shows the temperature acquisition system designed for recording temperature variation with time during spray cooling. Signals measured by the inserted
thermocouples are amplified and filtered using a 5B37 thermocouple module and passed to the PCI-MIO-16E-4 board (National Instruments). The AI Config VI configures the different parameters of the acquisition, such as the channels to be read and the size of the buffer to use. The Start VI specifies parameters to start the acquisition, such as number of scans to acquire, the rate at which this VI takes the data, and the trigger settings. The AI Read VI specifies parameters to retrieve the data from the data acquisition buffer. The retrieved data is passed to the transposed waveform graph and also saved in a file on the hardware of the computer. Finally, the AI Clear VI is called to deallocate all buffers and other sources used for the acquisition by invalidating the taskID. If an error occurs in any of these VIs, the program passes the error through the remaining VIs to the Simple Error Handler VI, which notifies the user of the error.
Figure A.1  Diagram of the DAC system for single droplet boiling.
Figure A.2  Diagram of the camera control system for spray cooling.
Figure A.3  Diagram of the DAC system for spray cooling.
Appendix B  Physical Properties of Electrolyte Solutions

The study on boiling of droplets containing dissolved salts requires reasonably accurate calculations of the physical properties of the electrolyte solutions. The physical properties involved in this study include vapor pressure, viscosity, surface tension, solubility. Variations of these properties are determined as follow.

B.1  Vapor Pressure

A vapor pressure equation for aqueous and non-aqueous solutions of single and mixed electrolytes proposed by Cisternas & Lam (1991) was used in this study. This correlation was examined for 176 systems (4157 experimental points). It gives results up to 44 mol kg\(^{-1}\) of ionic strength. Vapor pressure of electrolyte solutions can be calculated as:

\[
\log P = K I [A - B/(T - E_s)] + [C - D/(T - E_s)] 
\]

(B.1)

where

\[
A = A_s + 3.60591E - 4I + M_s/2303 \quad (B.2)
\]

\[
B = B_s + 1.382982I - 0.031185I^2 \quad (B.3)
\]

\[
C = C_s - 3.399334E - 3I - 1.11614E - 4I^2 + M_s I(1 - \chi)/2303 \quad (B.4)
\]

\[
D = D_s - 0.13848I + 0.027511I^2 - 1.79277E - 3I^3 \quad (B.5)
\]

\[
I = 0.5 \sum v_i Z_i^2 \quad (B.6)
\]

\[
\chi = 2(v_+ + v_-)/(v_+ Z_+^2 + v_- Z_-^2) \quad (B.7)
\]

In eqns. (B.1) – (B.5) \(P\) is the vapor pressure (kPa), \(T\) is the temperature (K), \(I\) is the ionic strength (mol kg\(^{-1}\)), \(M_s\) is the molecular weight of solvent, \(K\) is an electrolyte parameter and \(A_s, B_s, C_s, D_s\) and \(E_s\) are solvent parameters. In eqn. (B.7) \(v_s\) is the number
of moles of cation and \( v \) is the number of moles of anion produced by the dissociation of one mole of electrolyte, and \( Z^+ \) denotes the valency of cation and \( Z^- \) the valency of anion.

For water, the constants in the above equations are \( A_s=-0.0213302 \), \( B_s=-5.390915 \), \( C_s=7.192959 \), \( D_s=1730.2857 \) and \( E_s=39.53 \)

The K values of the electrolytes used in this study are shown in Table B.1. In this table \( N \) is the number of experimental data points, \( I_{\text{max}} \) is the maximum ionic strength, \( \Delta I \) shows the maximum and minimum temperatures in kelvins, \( \% \text{Av. Dev.} \) is the average percentage deviation.

\[
\%\text{Dev}_i = 100 \left| \frac{P_{\text{exp}_i} - P_{\text{cal}_i}}{P_{\text{exp}_i}} \right|
\]

(B.8)

\[
\%\text{Av. Dev.} = \frac{\sum_i \%\text{Dev}_i}{N}
\]

(B.9)

and \( \sigma \) is:

\[
\sigma = \frac{\sum_i |\%\text{Dev}_i - \%\text{Av. Dev.}|}{(N - 1)}
\]

(B.10)

Table B.1 K values and average percentage deviation of vapor pressure of aqueous solutions of single electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( N )</th>
<th>( \Delta T )</th>
<th>( I_{\text{max}} )</th>
<th>K</th>
<th>%Av. Dev.</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$</td>
<td>65</td>
<td>273-373</td>
<td>12</td>
<td>0.02497</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>9</td>
<td>373</td>
<td>10</td>
<td>0.15930</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>74</td>
<td>273-373</td>
<td>4</td>
<td>0.04490</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>NaCl</td>
<td>138</td>
<td>273-383</td>
<td>4</td>
<td>0.39015</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>4</td>
<td>373</td>
<td>12</td>
<td>0.03467</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The variations of vapor pressures of the electrolyte solutions used in this study were calculated and shown in Figure B.1.
B.2 Surface Tension

Surface tension of a multicomponent electrolyte solution can be calculated by the formula:

\[ \sigma = \sigma_0 + 0.049(1 - a_w) \]  \hfill (B.11)

where \( \sigma \) is the surface tension of the solution of a multicomponent electrolyte in N/m, \( \sigma_0 \) is the interface tension of water in N/m, \( a_w \) is water activity in multicomponent solution.

Surface tension of water can be determined from the equation:

\[ \sigma_0 = 0.2358[647.15 - T]/647.15 \pm 0.625(647.15 - T)/647.15 \]  \hfill (B.12)

Water activity in a multicomponent solution can be calculated as follows:

\[ \lg a_w = \sum_i (F_i + Q_i \sum_j m_j)m_i \]  \hfill (B.13)

where \( F_i, Q_i \) are coefficients, \( m_i \) is the solution molarity, a mole of substance dissolved in 1 kg of solvent.

The \( F_i \) and \( Q_i \) coefficients are calculated by the formula:

\[ F_i = f_{0i} + f_{1i} t + f_{2i} t^2 \]  \hfill (B.14)

\[ Q_i = q_{0i} + q_{1i} t + q_{2i} t^2 \]  \hfill (B.15)

The \( f_{mi} \) and \( q_{mi} \) obtained from the experiment data are listed in Table B.2.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(-f_{0i}.10^6)</th>
<th>(-f_{1i}.10^6)</th>
<th>(-f_{2i}.10^6)</th>
<th>(-g_{0i}.10^6)</th>
<th>(-g_{1i}.10^8)</th>
<th>(-g_{2i}.10^8)</th>
<th>(\Delta,%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
<td>46378.4</td>
<td>-211.79</td>
<td>0.92</td>
<td>-44450.9</td>
<td>5286.9</td>
<td>-38.26</td>
<td>2.26</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>39264.0</td>
<td>-67.57</td>
<td>-0.16</td>
<td>479582.3</td>
<td>-7074.5</td>
<td>2.66</td>
<td>2.66</td>
</tr>
<tr>
<td>NaCl</td>
<td>30552.5</td>
<td>-0.31</td>
<td>0.02</td>
<td>268677.1</td>
<td>-804.7</td>
<td>-0.17</td>
<td>2.89</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>17091.1</td>
<td>608.98</td>
<td>-7.06</td>
<td>389376.2</td>
<td>926.7</td>
<td>0</td>
<td>5.62</td>
</tr>
</tbody>
</table>
B.3 Viscosity

Dynamical viscosity coefficients can be calculated by the formula:

\[ \lg \eta = \lg \eta_0 + \sum_i (D_i c_i) \]  \hspace{1cm} (B.16)

where \( \eta \) is the viscosity of a multicomponent solution in Pa.s; \( \eta_0 \) is water viscosity in Pa.s; \( D_i \) are coefficients, \( c_i \) is the mass content of the component in kilograms of the substance per 1 kg of the solution.

Water viscosity can be determined from the Slott formula:

\[ \eta_0 = 0.59849(43.252 + t)^{-1.5423} \]  \hspace{1cm} (B.17)

where \( t=(0,100^\circ\text{C}) \), \( S_0=2.10^6 \) Pa.s

The \( D_i \) coefficients are calculated from dependences

\[ D_i = d_{0i} + d_{1i}t + d_{2i}t^2 \]  \hspace{1cm} (B.18)

The \( d_{ni} \) coefficients for the electrolytes used in this study are given in Table B.3. Variations of viscosity of the salts used in this study with concentration at the temperature of 100°C are shown in Figure B.2.

Table B.2 Coefficients in Eq. B.18 for viscosity

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( d_{0i} \times 10^2 )</th>
<th>( d_{1i} \times 10^4 )</th>
<th>( d_{2i} \times 10^5 )</th>
<th>( S_n \times 10^6 ) Pa c</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>307.9</td>
<td>-0.1</td>
<td>0</td>
<td>2389</td>
</tr>
<tr>
<td>( \text{NaHCO}_3 )</td>
<td>94.2</td>
<td>18.2</td>
<td>0</td>
<td>2181</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_4 )</td>
<td>141.8</td>
<td>9.9</td>
<td>0</td>
<td>855</td>
</tr>
<tr>
<td>( \text{NaCl} )</td>
<td>71.8</td>
<td>35.9</td>
<td>0</td>
<td>1340</td>
</tr>
<tr>
<td>( \text{MgSO}_4 )</td>
<td>272.9</td>
<td>-53.5</td>
<td>0</td>
<td>1354</td>
</tr>
</tbody>
</table>
B.4 Solubility

No practical correlations are available for calculation of viscosity. Variations of the solubility of the electrolytes used in this study with temperature were obtained from literature and shown in Figure B.3.
Figure B.1 Variations of vapor pressures of the electrolyte solutions with increasing mass concentration at 100°C.
Figure B.2  Variation of viscosity of the salts used in the experiments with increasing mass concentration at 100°C.
Figure B.3 Variations of solubility of the electrolytes with increasing solution temperature.
Appendix C  Determination of Carbon Dioxide Concentration in Water

Determination of the amount of dissolved gas has been carried out by various physical and chemical methods. Many different physical methods for determining the solubility of gases in liquids were described in earlier reviews. Basically, physical methods may be divided into two broad classification: saturation methods wherein a previously degasses solvent is saturated with a gas under conditions in which the necessary pressures, volume, and temperatures may be determined; and extraction methods wherein the dissolved gas in previously saturated solution is removed under conditions in which the pressure, volume, and temperature may be determined. Equilibrium saturation conditions have been attained for the gas and liquid phases by shaking a mixture of the two, by flowing a thin film of liquid through the gas, by bubbling (usually via a fritted disc) the gas through the liquid, or by flowing the gas over the liquid while it is held stationary on some supporting medium (as in gas-liquid partition chromatography).

In this study, a Natelson Microgasometer (Model #650), which is shown in Figure C.1, was employed to measure carbon dioxide concentration in water. This Natelson Microgasometer adapts the classical Van Slyke manometric method to ultra-micro analysis. This manometric apparatus is based on the principle of extraction of gases from the liquid by shaking the liquid in a relatively large free space in a Torricellian vacuum and subsequent measurement of the pressure of the liberated gas after reducing the volume of the extracted gas to a limited volume. A certain portion of the dissolved gas remains unextracted and can be calculated to correct the total volume of the dissolved gas measured from the extracted gas.
**Operation procedures for determination of CO₂**

Advance the mercury until a small drop is held on the tip of the pipette. Draw in from each vial as follows:

1) Sample — 0.03 ml. of liquid and 0.01 to 0.02 ml. of mercury.

2) Lactic Acid — 0.03 lactic acid and 0.01 ml. of caprylic alcohol followed by 0.1 ml. of mercury.

3) Water — 0.1 ml. of distilled and degassed water, follow with mercury to the 0.12 ml. mark of reaction chamber.

Manipulate controls as follows:

4) Close the reaction chamber stopcock and retreat with piston until liquid level is halfway into reaction chamber.

5) Loosen clamping knob and shake for one minute.

6) Advance piston till the top aqueous meniscus is at the 0.12 ml. mark.

7) Record manometer reading \( P₁ \) and temperature.

8) Advance piston till mercury is at top of manometer.

9) Hold NaOH vial under pipette and open reaction chamber stopcock.

10) Adjust mercury if necessary until drop is at tip of pipette.

Draw in from NaOH vial as follows:

11) 0.03 ml. of NaOH and mercury to 0.12 ml. mark.

Manipulate controls as follows:

12) Close reaction chamber stopcock and retreat with piston. Shake for one minute until liquid level is halfway into reaction chamber.

13) Advance piston till aqueous meniscus is at 0.12 ml. mark.

14) Record manometer reading \( P₂ \).

Calculate results:
15) CO\(_2\) content = (P\(_1\) - P\(_2\)) multiplied by the factor for temperature.

**Calculation of CO\(_2\) concentration**

The total CO\(_2\) content of the solution analyzed is obtained by reducing the volume of CO\(_2\) extracted to standard conditions by multiplication with the usual factor \(\frac{(B - w)273}{760T}\), and adding the volume to correct the volume \(x\) of CO\(_2\) remaining in solution.

\[
V_{0^\circ,760} = a \frac{B - w}{760} \times \frac{273}{T} + x
\]  
(C.1)

where

\(a\) = volume of CO\(_2\) obtained by one extraction and measured at atmospheric conditions of \(t^\circ\) temperature and B mm, barometric pressure. (0.12 ml.)

\(T\) = the room temperature in K.

\(B-w\) = the barometric pressure corrected for \(w\), the vapor tension of water.

Since the volume \(x\) of gas dissolved is proportional to its partial pressure \(p\), solubility \((\alpha_{CO2})\), and the volume of the solvent \(S\), the volume \(x\) of CO\(_2\) remaining in solution can be expressed as:

\[
x = \frac{p}{760}S\alpha_{CO2}
\]  
(C.2)

where

\(S\) = Total volume of solution from which gas is extracted (0.17 ml.).

Since pressure varies inversely with gas volume,

\[
\frac{p}{B-w} = \frac{a}{A-S}
\]  
(C.3)

thus

\[
p = (B - w) \frac{a}{A-S}
\]  
(C.4)
where

\[ A = \text{Volume of chamber occupied by gas and solution (3 ml.)} \]

\[ A-S = \text{Volume of gas during extraction.} \]

Substituting this value into Eq. (C.2) and then the value of \( x \) into Eq. (C.1) gives:

\[ V_{0^\circ,760} = a \frac{B-w}{760} \left( \frac{273}{T} + \frac{S\alpha_{CO_2}}{A-S} \right) \]  \hspace{1cm} (C.5)

Since \( \alpha_{CO_2} = \alpha_{CO_2}' \frac{273}{T} \), Eq. C.5 may be expressed as:

\[ V_{0^\circ,760} = a \frac{B-w}{760} \times \frac{273}{T} (1.0 + \frac{S}{A-S} \alpha_{CO_2}') \]  \hspace{1cm} (C.6)

or

\[ V_{0^\circ,760} = a \frac{B-w}{760(1 + 0.00367t)} (1.0 + \frac{S}{A-S} \alpha_{CO_2}') \]  \hspace{1cm} (C.7)

where \( \alpha_{CO_2}' \) is the Bunsen solubility coefficient.

Substitution of \( B-w \) with \( P \) into Eq. C.7 gives:

\[ V_{CO_2,760} = a \times \frac{P}{760} \times \frac{1}{1 + 0.00367t} \times (1.0 + \frac{S\alpha_{CO_2}'}{A-S}) \]  \hspace{1cm} (C.8)

where

\[ P = \text{Observed pressure.} \]

\[ t = \text{Temperature in °C.} \]

Due to reabsorption of extracted CO\(_2\) while the volume is being reduced from \( A-S \) to the volume at which gas is measured \( (a) \), this equation has to be corrected. Indicating as \( i \), a factor must be multiplied in order to correct for reabsorption, we have

\[ V_{CO_2,760} = a \times \frac{P}{760} \times \frac{1}{1 + 0.00367t} \times (1.0 + \frac{S\alpha_{CO_2}'}{A-S}) \times i \]  \hspace{1cm} (C.9)

where

\[ i = \text{Correction factor for reabsorption of gas (1.060).} \]
In addition, the temperature effect on the specific gravity of mercury must be included.

The temperature for reading a barometric column on a glass scale, according to Landolt-Bornstein's "Tabellen", 0.000172 t mm. for each millimeter in height of the barometric column. Introducing this correction, Eq. C.9 becomes

\[ V_{CO_2,760} = a \times \frac{P}{760} \times \frac{1 - 0.000172t}{1 + 0.00367t} \times (1.0 + \frac{S\alpha_{CO_2}}{A - S})i \] (C.10)

Simplifying Eq. C.10 by discarding negligible decimals in the resulting coefficients of \( t \) yields:

\[ V_{CO_2,760} = a \times \frac{P}{760} \times \frac{1}{1 + 0.00384t} \times (1.0 + \frac{S\alpha_{CO_2}}{A - S})i \] (C.11)

The concentration of dissolved CO\(_2\) can be expressed as follows:

\[ C_{CO_2,760} = \frac{1}{S} \times a \times \frac{P}{760} \times \frac{1 - 0.000172t}{1 + 0.00367t} \times (1.0 + \frac{S\alpha_{CO_2}}{A - S})i \quad \text{(ml/ml)} \] (C.12)
Figure C.1  Natelson Microgasometer (Model #650, Scientific Industries, Inc.)
Appendix D  Decomposition rate of Sodium Bicarbonate

The decomposition reaction 2NaHCO₃ (s) → Na₂CO₃ (s) + H₂O (g) + CO₂ (g) is highly dependent on temperature. Hu et al. (1986) reported that the decomposition was first order in mass of NaHCO₃. The decomposition rate can be calculated by the following correlation (Hu et al., 1986).

\[ \ln\left(\frac{W}{W_0}\right) = -k_d t \]  

(D.1)

where \( W \) is the mass of NaHCO₃ at any time, \( W_0 \) is the initial mass of NaHCO₃, \( t \) is the reaction time, and \( k_d \) is the decomposition rate (s⁻¹). \( k_d \) can be calculated in Arhenius equation:

\[ k_d = k_0 \exp\left(-\frac{E}{R_T}\right) \]  

(D.2)

where \( k_0 \) is the pre-exponential factor of decomposition, 1.43 x 10¹¹ s⁻¹; \( E \) is the activation energy, 102 kJ/mol. The decomposition rate \( k_d \) is very fast at temperature above 400K (123°C). The amount of NaHCO₃ decomposing during droplet evaporation and CO₂ produced from the decomposition process were calculated and shown in Figure D.1 and Figure D.2, respectively.
NaHCO₃ decomposing at the end of evaporation (kg/kg initial NaHCO₃)

Surface Temperature (°C)

Figure D.1: The amount of NaHCO₃ decomposing during boiling of a water droplet on a hot surface at temperatures ranging from 100°C to 210°C.
Figure D.2  Production rate of CO$_2$ (kg/kg) during boiling of a droplet containing NaHCO$_3$ on a hot surface at temperatures ranging from 100°C to 210°C.
Appendix E  Computer Programs

*  E.1 PROPERTY.FOR

******************************************************************************

*  Calculate Vapor Partial Pressure, Surface Tension and Viscosity of Electrolyte
*  Solutions

******************************************************************************

*  PARAMETER(ID=18)
  INTEGER I,IB,IE,IDATI,IDATO
  REAL T[ID]
  REAL A, B, C, D, E
  REAL As, Bs, Cs, Ds, Es, Ms, K, MWS
  REAL X
  REAL f0,f1,f2,q0,q1,q2
  REAL d0,d1,d2
  INTEGER VP, VN, ZP, ZN
  REAL P[ID],CONCENT[ID],ION[ID],ST0[ID],ST[ID]
  REAL TBP[ID],VIS[ID]

*  CALL FILDEF(IDATI,IDATO)
  CALL INPUT(IB,IE,ID,As, Bs, Cs, Ds, Es, Ms, K, MWS, VP, VN, ZP, ZN,
  CALL ECHO(IB,IE,ID,As, Bs, Cs, Ds, Es, Ms, K, MWS, VP, VN, ZP, ZN,
  CALL SURFACETENSION(IB,IE,ID,f0,f1,f2,q0,q1,q2,MWS,CONCENT,T,ST0,
  CALL BOILINGPOINT(IB,IE,ID,d0,d1,d2,MWS,CONCENT,TBP,IDATO)
  CALL VISCOSITY(IB,IE,d0,d1,d2,MWS,CONCENT,FR)
  WRITE(IDAT0,100)
  WRITE(IDATO,101)(T(I),ION(I),P(I),ST0(I),ST(I),TBP(I),VIS(I),CONCENT(I),
  FORMAT(1X,F7.3,4X,F8.5,4X,F12.5,2XF12.5,2X,
  101 FORMAT(1X,F7.3,4X,F8.5,4X,F12.5,2X,F12.5,2X,F12.5,2X,)
C     F12.5,2X,F12.5,2X,F12.5)
     STOP
     END

********************************************************************************************
*  File: input.f contains 3 subroutines: FILDEF, INPUT and ECHO
********************************************************************************************

SUBROUTINE FILDEF(IDATI, IDATO)
*
*  Subroutine to define unit numbers and open data files.
*  INTEGER IDATI  unit number for file with formatted input data; input
*  INTEGER IDATO  unit number for file with formatted output; output
********************************************************************************************

INTEGER IDATI, IDATO
*
*
FILE UNIT NUMBERS
*

IDATI=71
IDATO=72
*

OPEN(IDATI,FILE='in.dat')
OPEN(IDATO,FILE='out.dat')
RETURN
END
*

********************************************************************************************

SUBROUTINE INPUT(IB,IE,ID,As, Bs, Cs, Ds, Es, Ms, K, MWS, VP, VN, ZP,
     ZN, f0,f1,f2,q0,q1,q2,d0,d1,d2,IDATI)
*
*
Subroutine to read input variable from a data file
*
INTEGER IB,IE  first and last data indices in i; output
*
INTEGER ID,    the total number of experiment data set
*
REAL T(ID)   the temperature of the electrolyte solution; output
*
REAL As, Bs, Cs, Ds, Es   the parameters of the solvent; output
*
REAL Ms   the molecular weight of the solvent; output
*
REAL K    an electrolyte parameter; output
*
REAL CONCENT   the concentration (mass) of the solution; output
*
REAL VP    the number of moles of cation produced by dissociation
*
     of one mole of the electrolyte; output
REAL VN    the number of moles of anion produced by dissociation
REAL ZP    the valency of cation; output
REAL ZN    the valency of anion; output
INTEGER IDATI unit number for file with formatted input data; input

INTEGER I,IB,IE,IDATI
REAL As, Bs, Cs, Ds, Es, Ms, K, MWS
INTEGER VP, VN, ZP, ZN
REAL f0,f1,f2,q0,q1,q2,d0,d1,d2

IB=1
IE=ID

Set the initial values as zero
As=0.0
Bs=0.0
Cs=0.0
Ds=0.0
Es=0.0
Ms=0.0
K=0.0
VP=0.0
VN=0.0
ZP=0.0
ZN=0.0
f0=0.0
f1=0.0
f2=0.0
q0=0.0
q1=0.0
q2=0.0
d0=0.0
d1=0.0
d2=0.0

READ(IDATI, 5000) As, Bs, Cs, Ds, Es, Ms,K, MWS, VP, VN, ZP, ZN
5000 FORMAT(F12.9,F12.9,F12.9,F12.6,F9.4,F7.3,F10.7,F8.3,I3,I3,I3,I3)
READ(IDATI,5001) f0,f1,f2,q0,q1,q2
5001 FORMAT(6E14.4)
   READ(IDATI,5002) d0,d1,d2
5002 FORMAT(3E14.4)
   RETURN
END

*  

**************************************************************************
INTEGER I,IB,IE,IDATO
REAL As, Bs, Cs, Ds, Es, Ms, K, MWS
INTEGER VP, VN, ZP, ZN
REAL f0,f1,f2,q0,q1,q2,d0,d1,d2
WRITE(IDATO,6000) IB,IE,ID
WRITE(IDATO,6020)
WRITE(IDATO,6030) As, Bs, Cs, Ds, Es, Ms
WRITE(IDATO,6040) K, MWS, VP, VN, ZP, ZN
WRITE(IDATO,6050) d0,d1,d2
6000 FORMAT(' IB=',I3,' IE=',I3,' ID=',U)
6020 FORMAT(/,' As',' Bs',' Cs',' Ds,'
       C  ' Es',' Ms')
6021 FORMAT(/, ' K',' MWS',' VP',' VN',' ZP',' ZN')
6030 FORMAT(2X,F12.9,2X,F12.9,2X,F12.9,2X,F12.9,2X,F12.6,2X,F9.4,2X,F7.3)
6040 FORMAT(/, ' f0', ' f1', ' f2',
       C  ' q0', ' q1', ' q2')
6041 FORMAT(6(2X,E14.4))
6050 FORMAT(2X, ' d0',2X, ' d1',2X, ' d2')
6051 FORMAT(3(2X,E14.4))
   RETURN
SUBROUTINE VAPPRESSURE(IB, IE, ID, As, Bs, Cs, Ds, Es, Ms, K, MWS, VP, C, VN, ZP, ZN, CONCENT, ION, T, P, IDATO)

* Subroutine to calculate the vapor partial pressure of the electrolyte solution
* REAL ION the ionic strength of the solution; output
* REAL P(ID) vapor partial pressure of the solution; output
* REAL T(ID) the temperature of the solution; output
* See INPUT file for other variable parameters

INTEGER I, IB, IE, IDATO
REAL A, B, C, D, Z, X
REAL As, Bs, Cs, Ds, Es, Ms, K, MWS
REAL ION(ID)
INTEGER VP, VN, ZP, ZN
REAL T(ID)
REAL P(ID), CONCENT(ID)

DO 600 I = IB, IE
IF(I.EQ.1) THEN
   CONCENT(I) = 0.0
ELSE
   CONCENT(I) = (I-1)*0.02
END IF
ION(I) = 0.5*(VP*ZP**2+VN*ZN**2)*CONCENT(I)/MWS*1000.0
X = 2.0*(VP+VN)/(VP*ZP**2+VN*ZN**2)
A = As+3.60591E-4*ION(I)+Ms/2303.0
B = Bs+1.382982*ION(I)-0.031185*ION(I)**2
C = Cs-3.99334E-3*ION(I)-1.11614E-4*ION(I)**2+Ms*ION(I)*(1-X)/2303.0
D = Ds-0.138481*ION(I)+0.027511*ION(I)**2-1.79277E-3*ION(I)**3

T(I) = 273+100.0
P(I) = 10**((K*ION(I))*(A-B/(T(I)-Es))+(C-D/(T(I)-Es)))
CONTINUE
WRITE(IDATO, 200) X
**File surfacetension.f**

**SUBROUTINE SURFACETENSION**

```fortran
INTEGER I,B,I,E,IDATO
REAL f0,f1,f2,q0,q1,q2,MWS
REAL T(ID)
REAL FI,QI,aw
REAL ST0(ID),ST(ID),CONCENT(ID)
REAL m

DO 700 I=IB,IE
IF(I.EQ.1) THEN
   CONCENT(I)=0.01
ELSE
   CONCENT(I)=(I-1)*0.02
END IF

m=CONCENT(I)/MWS*1000.0
T(I)=273.15+100.0
ST0(I)=0.2358*((647.15-T(I))/647.15)**1.256*(1.0-0.625*(647.15-T(I))/647.15)
FI=f0+f1*(T(I)-273.15)+f2*(T(I)-273.15)**2
QI=q0+q1*(T(I)-273.15)+q2*(T(I)-273.15)**2
aw=EXP((FI+QI*m)*m)
ST(I)=ST0(I)+0.049*(1-aw)
```

* Subroutine to calculate the surface tension of the electrolyte solution
* REAL f0,f1,f2,q0,q1,q2 the parameters of the salt; input
* REAL ION the ionic strength of the solution; output
* REAL ST0(ID) the surface tension of the solution; output
* REAL ST(ID) the surface tension of the solution; output
* REAL T(ID) the temperature of the solution; output
* See INPUT file for other variable parameters
CONTINUE
RETURN
END

************************************************************************
* File boilingpoint.f
************************************************************************

SUBROUTINE BOILINGPOINT(IB,IE,ID,f0,f1,f2,q0,q1,q2,MWS,CONCENT,
C
TBP,IDATO)
*
* Subroutine to calculate the surface tension of the electrolyte solution
* REAL f0,f1,f2,q0,q1,q2 the parameters of the salt; input
* REAL ION the ionic strenght of the solution; output
* REAL ST0(ID) the surface tension of the solution; output
* REAL ST(ID) the surface tension of the solution; output
* REAL T(ID) the temperature of the solution; output
* REAL TBP(ID) the boiling point of the solution; output
* See INPUT file for other variable parameters
************************************************************************

INTEGER I,IB,IE,IDATO
REAL f0,f1,f2,q0,q1,q2,MWS
REAL FI,QI,aw
REAL TBP(ID),CONCENT(ID)
REAL m
REAL Pp
*

Pp=1.01332E+5
*

DO 700 I=IB,IE
IF(I.EQ.1) THEN
CONCENT(I)=0.01
ELSE
CONCENT(I)=(I-1)*0.02
END IF
*

m=CONCENT(I)/MWS*1000.0
BP=373.15
120 FI=f0+f1*(BP-273.15)+f2*(BP-273.15)**2
QI=q0+q1*(BP-273.15)+q2*(BP-273.15)**2
aw=EXP((FI+QI*m)*m)

TBP(I)=329.6509/((10.712539+ALOG(aw*1E+05/Pp))**0.5*2.388819)

IF (ABS(((TBP(I)-BP)/BP).GT.0.005) THEN
BP=(TBP(I)+BP)/2.0
GO TO 120
ELSE
TBP(I)=BP
END IF
700 CONTINUE
RETURN
END

************************************************************************
* File viscosity.f
************************************************************************

SUBROUTINE VISCOSITY(IB,IE,ID,dO,dl,d2,MWS,CONCENT,VIS,T,IDATO)
*
* Subroutine to calculate the viscosity of the electrolyte solution
* REAL dO,dl,d2 the parameters of the salt; input
* REAL ION the ionic strength of the solution; output
* REAL ST0(ID) the surface tension of the solution; output
* REAL ST(ID) the surface tension of the solution; output
* REAL T(ID) the temperature of the solution; output
* REAL TBP(ID) the boiling point of the solution; output
* See INPUT file for other variable parameters
************************************************************************
INTEGER I,IB,IE,IDATO
REAL dO,dl,d2,MWS
REAL VIS0,D
REAL VIS(ID),T(ID),CONCENT(ID)
*
DO 700 I=IB, IE
IF(I.EQ.1) THEN
CONCENT(I)=0.01
ELSE
CONCENT(I)=(I-1)*0.02
END IF
T(I)=373.15
VIS0=0.59849*(43.252+(T(I)-273.15))**(-1.5423)
D=d0+d1*(T(I)-273.15)+d2*(T(I)-273.15)**2

VIS(I)=10**(ALOG10(VIS0+D*CONCENT(I)))

700 CONTINUE
RETURN
END
* E2 TEMPERATURE.FOR
*************************************************************************
* CONVERT THE ACQUIRED DATA OF VOLTAGES INTO TEMPERATURES
* INTEGER ID, THE MAXIMUM OF DATA; INPUT
*************************************************************************
* PARAMETER(ID=33000)
INTEGER I,IB,IE,IDATI,IDATO
INTEGER SCANRATE
*
REAL VOLT1(ID),VOLT2(ID),VOLT3(ID),VOLT4(ID)
REAL TEMP1(ID),TEMP2(ID),TEMP3(ID),TEMP4(ID)
REAL T1(ID),T2(ID),T3(ID),T4(ID)
REAL TIME(ID)
*
SCANRATE=100
*
CALL FILDEFWATI,DATO)
CALL INPUT(IB,IE,ID,VOLT1,VOLT2,VOLT3,VOLT4,IDATI)
CALL ECHO(IB,IE,ID,VOLT1,VOLT2,VOLT3,VOLT4,IDATO)
CALL TEMPERATURE(IB,IE,ID,SCANRATE,TIME,VOLT1,VOLT2,
C VOLT3,VOLT4,TEMP1,TEMP2,TEMP3,TEMP4,IDATO)
CALL NOISEREMOVE(IB,IE,ID,SCANRATE,TEMP1,TEMP2,TEMP3,
C TEMP4,T1,T2,T3,T4)
WRITE(IDATO,10)
WRITE(IDATO,20) (TIME(I),TEMP1(I),TEMP2(I),TEMP3(I),TEMP4(I), I=IB,IE)
10 FORMAT(/, 'TIME(s)', 'TEMP1(C)', 'TEMP2(C)',
C 'TEMP3(C)', 'TEMP4(C)')
STOP
END

* -----------------------------------------------
* File:input.f contains 3 subroutines: FILDEF, INPUT and ECHO
* 
* -----------------------------------------------
*
SUBROUTINE FILDEF(IDATI, IDATO)
 *
 * Subroutine to define unit numbers and open data files.
 * INTEGER IDATI  unit number for file with formatted input data; input
 * INTEGER IDATO  unit number for file with formatted output; output
 *
******************************************************************************
 INTEGER IDATI, IDATO
 *
* FILE UNIT NUMBERS
*

 IDATI=71
 IDATO=72

 OPEN(IDATI,FILE='in.dat')
 OPEN(IDATO,FILE='out.dat')
 RETURN
 END

******************************************************************************
 *
 SUBROUTINE INPUT(IB,IE,ID,VOLT1,VOLT2,VOLT3,VOLT4,IDATI)
 *
 * Subroutine to read input variable from a data file
 *
 * INTEGER IB,IE  first and last data indices in i; output
 * INTEGER ID,  the total number of experiment data set
 * REAL VOLT1(ID)  the voltage of the first thermocouple; input
 * REAL VOLT2(ID)  the voltage of the first thermocouple; input
 * REAL VOLT3(ID)  the voltage of the first thermocouple; input
 * REAL VOLT4(ID)  the voltage of the first thermocouple; input
 * INTEGER IDATI unit number for file with formatted input data; input
 *
******************************************************************************
 *
 INTEGER I,IB,IE,ID,IDATI
 REAL VOLT1(ID),VOLT2(ID),VOLT3(ID),VOLT4(ID)
 *
 IB=1
IE=ID

* Set the initial values as zero
DO 81 I=IB,IE
  VOLT1(I)=0.0
  VOLT2(I)=0.0
  VOLT3(I)=0.0
  VOLT4(I)=0.0
81 CONTINUE

* READ(IDATI, 50) (VOLT1(I),VOLT2(I),VOLT3(I),VOLT4(I),I=IB,IE)
50 FORMAT(4(1X, F8.6))

* RETURN
END

*************************************************************************
INTEGER I,IB,IE,ID,IDATO
REAL VOLT1(ID),VOLT2(ID),VOLT3(ID),VOLT4(ID)

* WRITE(IDATO, 60) IB,IE,ID
WRITE(IDATO, 62)
WRITE(IDATO, 63) (VOLT1(I),VOLT2(I),VOLT3(I),VOLT4(I),I=IB,IE)
60 FORMAT(' IB=',I3,' IE=',I3,' ID=',I3)
62 FORMAT(/,' VOLT1(mV)', ' VOLT2(mV)', ' VOLT3(mV)', ' VOLT4(mV)')
63 FORMAT(4(2X,F8.6))

RETURN

*************************************************************************
SUBROUTINE TEMPERATURE(IB,IE,ID,SCANRATE,TIME,VOLT1,VOLT2, VOLT3,VOLT4,TEMP1,TEMP2,TEMP3,TEMP4,IDATO)

* Subroutine to CONVERT VOLTAGE TO TEMPERATURE
* DOUBLE PRECISION C0,C1,C2,C3,C4,C5,C6,C7,C8; input
* INTEGER SCANRATE scan rate of the device; input
* REAL TEMP1(ID),TEMP2(ID),TEMP3(ID),TEMP4(ID) converted
* temperature; output
* REAL TIME(ID) acquiring time; output

INTEGER I,IB,IE,IDATO
DOUBLE PRECISION C0,C1,C2,C3,C4,C5,C6,C7,C8
INTEGER SCANRATE
REAL V

REAL VOLT1(ID),VOLT2(ID),VOLT3(ID),VOLT4(ID)
REAL TEMP1(ID),TEMP2(ID),TEMP3(ID),TEMP4(ID)
REAL TIME(ID)

* calibration constant of the temperature vs voltage curve
* taken from the Omega temperature handbook

C0= 0.226584602
C1= 24152.10900
C2= 67233.4248
C3= 2210340.682
C4= 860963914.9
C5= 4.83506E10
C6= -1.18452E12
C7= 1.38690E13
C8= -6.33708E13

DO 10 I=IB,IE
   TIME(I)=(I-1)*1.0/SCANRATE
   V=(VOLT1(I)/0.086688-3.553-0.05188)/1000.0
TEMP1(I)=C0 + (C1*V) + (C2*V**2) + (C3*V**3) + (C4*V**4) + (C5*V**5) + (C6*V**6) + (C7*V**7) + (C8*V**8) + (C9*V**9) + (C10*V**10) + (C11*V**11) + (C12*V**12) + (C13*V**13)

V=(VOLT2(I)/0.086688-3.553-0.05188)/1000.0

TEMP2(I)=C0 + (C1*V) + (C2*V**2) + (C3*V**3) + (C4*V**4) + (C5*V**5) + (C6*V**6) + (C7*V**7) + (C8*V**8) + (C9*V**9) + (C10*V**10) + (C11*V**11) + (C12*V**12) + (C13*V**13)

V=(VOLT3(I)/0.086688-3.553-0.05188)/1000.0

TEMP3(I)=C0 + (C1*V) + (C2*V**2) + (C3*V**3) + (C4*V**4) + (C5*V**5) + (C6*V**6) + (C7*V**7) + (C8*V**8) + (C9*V**9) + (C10*V**10) + (C11*V**11) + (C12*V**12) + (C13*V**13)

V=(VOLT4(I)/0.086688-3.553)/1000.0

TEMP4(I)=C0 + (C1*V) + (C2*V**2) + (C3*V**3) + (C4*V**4) + (C5*V**5) + (C6*V**6) + (C7*V**7) + (C8*V**8) + (C9*V**9) + (C10*V**10) + (C11*V**11) + (C12*V**12) + (C13*V**13)

V=(VOLT5(I)/0.086688-3.553)/1000.0

10 CONTINUE
WRITE(IDATO,11) VOLT1(1), SCANRATE, TIME(2)
11 FORMAT(F8.6,I4)
RETURN
END

INTEGER IB,IE,ID,iJ,k
INTEGER n9,nmax
REAL sum1,sum2,sum3,sum4
REAL avg1,avg2,avg3,avg4
REAL TEMP1(ID),TEMP2(ID),TEMP3(ID),TEMP4(ID)
REAL T1(ID),T2(ID),T3(ID),T4(ID)
REAL time
INTEGER SCANRATE

***At each time step, this program will take the average of 10 data points, including the current temperature and 9 future temperatures and assign the average as the current temperature value to remove any noise and smooth the curve***

SUBROUTINE NOISEREMOVE(IB,IE,ID,SCANRATE,TEMP1,TEMP2,TEMP3, TEMP4,T1,T2,T3,T4)

INTEGER IB,IE,ID,i,j,k
INTEGER n9,nmax
REAL sum1,sum2,sum3,sum4
REAL avg1,avg2,avg3,avg4
REAL TEMP1(ID),TEMP2(ID),TEMP3(ID),TEMP4(ID)
REAL T1(ID),T2(ID),T3(ID),T4(ID)
REAL time
INTEGER SCANRATE
c open a new output file

    open(unit=40,file='output',status='new')

c initiate the moving average routine

    nmax=ID
    n9=nmax-49
    do 2 j=1,n9
        sum1=0
        sum2=0
        sum3=0
        sum4=0
        do 4 i=j,j+49
            sum1=sum1 + TEMP1(i)
            sum2=sum2 + TEMP2(i)
            sum3=sum3 + TEMP3(i)
            sum4=sum4 + TEMP4(i)
        4 continue

    c taking the average of (10) ten data points at a time

    avg1=sum1/50
    avg2=sum2/50
    avg3=sum3/50
    avg4=sum4/50
    T1(j)=avgl
    T2(j)=avg2
    T3(j)=avg3
    T4(j)=avg4

2 continue

c initiate the time table

    time=0.0

c initiate the routine of writing out the averaged surface temperature versus a time table

    do 8 k=1,n9,50
c format the output file

    write (40,5) time, T1(k), T2(k), T3(k), T4(k)
5 format(1x,f12.5,2x,f5.1,2x,f5.1,2x,f5.1,2x)

the time step is 10 times the sampling rate

time=time + 1.0/SCANRATE*50

continue

c close the output file
    close(unit=40)

return
    end

E3 IHCP.FOR

Program name: ihcp.for

This program estimates the surface heat flux history using transient temperature measurements inside the heat conducting body. This problem is called the inverse heat conduction problem, in contrast to the direct problem where the information at the surface is given. The IHCP is ill-posed problem which is characterized by extreme sensitivity of the surface heat flux to small variations in the interior temperatures. A function specification scheme which uses a Duhamel's theorem is utilized.

max--number of time steps taken before stopping
x(1)--position of the 1st thermocouple sensor
x(2)--position of the 2nd thermocouple sensor
x(3)--position of the 3rd thermocouple sensor
x(4)--position of the 4th thermocouple sensor
l--position of the insulated surface
dt--time step
ntc--number of thermocouples used
m--the mth time step
r--number of future heat flux involved in the calculation
t0--the initial conditions taken as uniform over the whole domain
f--the temperature dump due to a unit heat flux at the surface
q(m)--the estimated surface heat flux at m time step
time
timep--dimensionless time defined as alfa*time/1**2
ck(j,i)--the gain coefficients

dimension y(4,2500),ck(4,2500),tb(4,2500),f(4,2500),q(2500)
dimension x(4),xp(4),term(10)
real k,l
integer r
common k,l

open an existing output file
open(unit=10,file='in.dat',status='old')

open an output file
open(unit=20,file='output',status='unknown')

thermal diffusivity and conductivity of copper
alfa=117.e-6
k=401.

c positions of thermocouple relative to the top surface
c
x(1)=0.8e-3
x(2)=6.8e-3
x(3)=13.2e-3
x(4)=19.6e-3
l=32.8e-3

set grid size, time step etc
t0=240.
r=6
ntc=4
c read the temperature measurements
do 30 m=1,max
30 read(10,40)y(1,m),y(2,m),y(3,m),y(4,m)
40 format(15x,f5.1,2x,f5.1,2x,f5.1,2x,f5.1)
c
c forms gain coefficient ck(i,j)
sum=0.0
t=0.0
do 50 i=1,r
t=t+dt
tp=alfa*t/l**2
do 60 j=1,ntc
xp(j)=x(j)/l
call kern(xp(j),tp,f(j,i))
sum=sum+f(j,i)**2
60 continue
50 continue
do 70 i=1,r
do 80 j=1,ntc
ck(j,i)=f(j,i)/sum
80 continue
70 continue
c
c estimate the surface flux q(m) following a sequential order
c
time=0.0
do 100 m=1,max-r+i
q(m)=0.0
time=time+dt
tp=alfa*time/l**2
dtp=alfa*dt/l**2
do 110 j=1,ntc
do 120 i=1,r
call kern(xp(j),tp+(i-1)*dtp,f(j,m+i-1))
term(i)=0.0
do 130 n=1,m-1
130  term(i)=term(i)+q(n)*(f(j,m-n+i)-f(j,m-n+i-1))
tb(j,m+i-1)=term(i)+y(j,1)
q(m)=q(m)+ck(j,i)*(y(j,m+i-1)-tb(j,m+i-1))
120 continue
110 continue

qs=q(m)/1000000.
write(20,*)time,q(m)/k*x(1)+y(1,m),qs
100 continue

close(unit=10)
close(unit=20)
stop
End

This subroutine forms the kernel function \( f \), a temperature jump
due to a unit heat flux at the surface. \( f \) can also be referred
to as the influence function.

subroutine kern(x,t,f)
real k,l
common k,l
pi=2.*asin(1.)
  sum=t+1./3.-x+0.5*x**2
do 10 n=1,200
term=-2./pi**2/n**2*exp(-n**2*pi**2*t)*cos(n*pi*x)
  sum=sum+term
if (abs(term/sum).le.0.001) go to 50
10 continue
write(*,*)'does not converge'
stop
50  f=sum* 1/k
return
end